Simple Models for Predicting Electron Correlation

by

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A Thesis submitted to the

School of Graduate Studies

in partial fulfillment of the requirements for the degree of

Master of Science

Department of Chemistry

Memorial University of Newfoundland

August 2014

St. John’s Newfoundland

ABSTRACT

After almost a century since the postulation of quantum mechanics, the only chemical systems that can be treated exactly are those with one electron. For all many-electron problems we rely on approximate solutions to the electronic Schrödinger equation. The single largest error in the calculations is due to the lack of an accurate representation of what happens when two electrons come close together. How the motion of one electron is affected by that of the other electron is referred to as electron correlation. Not only is electron correlation a fundamental problem in quantum chemistry, it is also crucial in determining the important chemical effects.

The correlated motion of electrons with opposite spins, completely neglected in single-determinantal Hartree-Fock theory, remains as one of the central unsolved challenges in quantum chemistry. Simple models that can account for the missing correlation energy have been investigated for the isoelectronic atomic series of two to eighteen electrons in order to gain further insight into the form of a correlation operator. The strength of the electron correlation likely depends on both their separation in position space and their separation in momentum space; hence, it is expected that the correlation energy is related to the average inter-electron distance and to their kinetic energy. It has been previously shown that the average electron-electron distance is inversely proportional to the Coulomb energy; thus, the correlation energy was modelled as a function of Coulomb repulsion and kinetic energies. Additionally, application of the atomic correlation models to the modeling of the correlation energy for simple molecular systems have been explored.

ACKNOWLEDGEMENTS

Dr. Raymond Poirier for guidance, infinite and invariable support and understanding.

Dr. Dale Keefe for never-ever-ending motivation and encouragement and trust in me.

My ridiculously beautiful daughter Mora Helena for everlasting patience and inspiration.

Memorial University of Newfoundland, Chemistry Department, Cape Breton University, Chemistry Department, past and present members of the Computational Chemistry Research Group at Memorial University, and Molecular Spectroscopy Research Group at Cape Breton University.

Natural Sciences and Engineering Research Council Canada and Memorial University of Newfoundland for financial support.

The Atlantic Computational Excellence Network, regional high performance computing consortium for universities in Atlantic Canada, for computational resources.

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"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

Paul A. Dirac, Proceedings of the Royal Society of London. Series A.
Containing Papers of a Mathematical and Physical Character, Vol. 123, (1929)

"I believe in intuition and inspiration. … At times I feel certain I am right while not knowing the reason. When the eclipse of 1919 confirmed my intuition, I was not in the least surprised. In fact I would have been astonished had it turned out otherwise. Imagination is more important than knowledge. For knowledge is limited, whereas imagination embraces the entire world, stimulating progress, giving birth to evolution. It is, strictly speaking, a real factor in scientific research."

Albert Einstein, in "Cosmic Religion: With Other Opinions and Aphorisms" (1931)

“I think I can safely say that nobody understands quantum mechanics.”

Richard Feynman, in “The Character of Physical Law” (1965)

1. Theoretical Background

1.1. Introduction

Our physical world is composed of interacting many-particle systems. All possible information about a system is in principle contained in the many-body wavefunction, determined by the time-dependent Schrödinger equation. However the exact analytical solution to a many-particle problem is not possible. This many-body problem is not unique to quantum mechanics, but to all interacting particles or systems, such as galaxies, planets, electronic systems, or nuclear matter. The appropriate approximate solutions to numerous physical systems have been obtained using the ever developing theoretical and computational methods. In the heart of quantum chemistry it is the electronic many-body problem that the theoretical methods aim to solve. Great development and ample advances have been made in the theoretical chemistry field in the last 80 years; however, the main and the most important problem still remains: the accurate description of what happens when two or more electrons come close together, called the electron correlation. Not only is electron correlation a fundamental problem in quantum chemistry, it is also crucial in determining the important chemical effects.

1.2. Quantum Behavior of Atoms and Molecules

At the fundamental level, the chemistry of all atomic and molecular systems is determined by the physics of the electrons and nuclei of which they are composed. According to Dirac “The laws necessary for the mathematical treatment of a large part

of physics and the whole chemistry are accurately described by quantum mechanics, and are in essence completely known; the only difficulty lies in the fact that the application of these laws leads to the equations that are too complex to be solved."[1] The only chemical systems for which the electronic part of the Schrödinger equation can be solved exactly are the simplest one-electron systems, such as the hydrogen atom and the molecular hydrogen cation.[2] Since the birth of quantum mechanics and the postulation of the Schrödinger equation several methods to approximate the exact solutions to many-electron problems have been developed. Today, computational and theoretical chemistry have become irreplaceable in the modern scientific research. Their importance will be even more significant with the development of improved computational chemistry methods which could yield more accurate results in shorter computational time. With the exponential rise in computational power and resources we have experienced in the last few decades, the search for more advanced theoretical chemistry methods has become one of the most exciting and promising research topics.

The quantum behavior of atoms and molecules, in the absence of relativistic effects, is determined by the time-independent Schrödinger equation:

$$\hat{H}\Psi_n = E\Psi_n \tag{1.1}$$

where Ψ_n is the many-body wavefunction of the form:

$$\Psi_n \equiv \Psi_n(R_1, R_2, R_3, \dots ; r_1, r_2, r_3, \dots) \tag{1.2}$$

and $\hat{H}$ is the total Hamiltonian operator for the system of nuclei and electrons described by position vectors R_i and r_i, respectively, and representing the total energy, E, of all the particles of the system that can be written in atomic units as:[3]

$$\hat{H} = -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 + \sum_{\substack{A=1 \\ B>A}}^{M} \frac{Z_A Z_B}{|R_A - R_B|} - \sum_{\substack{i=1 \\ A=1}}^{N,M} \frac{Z_A}{|R_A - r_i|} + \sum_{\substack{i=1 \\ j>i}}^{N} \frac{1}{|r_i - r_j|} \quad (1.3)$$

where M_A is the ratio of the mass of nucleus A to the mass of an electron, and Z_A is the atomic number of nucleus A. The first two terms in the equation (1.3) are the kinetic energies for the nuclei and the electrons, respectively, where each Laplacian ∇_A^2 involves differentiation with respect to the nuclear coordinates of the A^{th} nucleus, while the ∇_i^2 term involves differentiation with respect to the coordinates of the i^{th} electron. The third, fourth and fifth terms in the equation (1.3) represent the potential energy of the system, and are the nuclear-nuclear repulsion, nuclear-electron attraction, and electron-electron repulsion energies, respectively. Analytical solutions to the time-independent Schrödinger equation are only possible for very simple systems; for the remainder of the problems one must rely on approximate models. Integration of equation (1.1) allows the energy to be expressed as an expectation value of the wavefunction, Ψ_n.[4]

$$E = \frac{\langle \Psi_n | \hat{H} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} \quad (1.4)$$

In the Born-Oppenheimer approximation, the electrons are assumed to be moving in a field of fixed nuclei because of their relative masses, and the total wavefunction can be approximated by the product of the electronic and nuclear wavefunctions.[5] The electronic Schrödinger equation can be written as:[6]

$$\hat{H}_{elec} \Psi_{elec}(\{r_i\}) = E_{elec} \Psi_{elec}(\{r_i\}) \quad (1.5)$$

where the electronic Hamiltonian $\hat{H}_{elec}$ in atomic units is.[3]

$$\widehat{H}_{elec}(r_1, r_2, r_3, \dots) = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|R_A - r_i|} + \sum_{\substack{i=1 \\ j>i}}^{N} \frac{1}{|r_i - r_j|} \tag{1.6}$$

The total energy of a system in a set of nuclear coordinates is the sum of the electronic energy and the nuclear repulsion energy, where the kinetic energy of the nuclei has been assumed to be zero. The energy dependence on the nuclear coordinates, a consequence of the Born-Oppenheimer approximation, gives rise to the potential energy surface (PES).[3]

1.3. Hartree-Fock Theory

In the Hartree-Fock (HF) approximation, the motion of an electron is determined by the attractive electrostatic potential of the nuclei and by the repulsive average field of all the other electrons of the system.[3] The HF approximate solution entails the wavefunction, Ψ_0, in the form of a single Slater determinant to describe the ground state of an *N*-electron system.[7-11]

$$\Psi_0(x_1, x_2, \dots, x_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \dots & \chi_N(x_N) \end{vmatrix} \tag{1.7}$$

Ψ_0 is the simplest antisymmetric product of the one-electron spin orbitals $\chi_i(x_i)$, $x_i = (\boldsymbol{r_i}, \omega_i)$, where x_i are the spatial and spin coordinates of each electron. The spin orbitals are products of spatial orbitals and spin functions, $\varphi(\boldsymbol{r})$ and $\alpha(\omega)$ or $\beta(\omega)$, respectively.[3] The electronic wavefunction in the form of a Slater determinant satisfies the antisymmetry principle, and also the indistinguishability of the electrons. The

expectation value of the electronic Hamiltonian and the Hartree-Fock wavefunction is the electronic Hartree-Fock energy.

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle \tag{1.8}$$

$$E_{HF\_e} = \sum_{i=1}^{N} \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_j \chi_i \rangle \tag{1.9}$$

where $\hat{h}$ is the one-electron operator:

$$\hat{h} = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} \tag{1.10}$$

and the $\langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_j \chi_i \rangle$ are two-electron integrals. The orthonormality constraint of the spin orbitals is written as:

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}, \qquad \forall\, i, j \tag{1.11}$$

The HF equations are derived by minimizing the energy expression with respect to the spin orbitals. The expression for the total HF energy, including the nuclear repulsion energy of a 2*N*-electron system with closed shells is given by:[3]

$$E_{HF} = 2 \sum_{a=1}^{N} H_{aa} + \sum_{a=1}^{N} \sum_{b=1}^{N} (2J_{ab} - K_{ab}) + V_{NN} \tag{1.12}$$

where H_{aa} is the one-electron energy,

$$H_{aa} = \langle \varphi_a | \hat{h} | \varphi_a \rangle = \langle a | \hat{h} | a \rangle \tag{1.13}$$

J_{ab} is the two-electron energy given by the Coulomb integral, $\langle ab|ab \rangle$,

$$J_{ab} = \iint \varphi_a^*(r_1)\, \varphi_b^*(r_2) \frac{1}{r_{12}} \varphi_a(r_1) \varphi_b(r_2) dr_1 dr_2 \tag{1.14a}$$

K_{ab} is the two-electron energy given by the exchange integral, $\langle ab|ba \rangle$,

$$K_{ab} = \iint \varphi_a^*(r_1)\,\varphi_b^*(r_2)\frac{1}{r_{12}}\varphi_b(r_1)\varphi_a(r_2)dr_1dr_2 \qquad (1.14b)$$

and V_{NN} is the nuclear repulsion term. The closed-shell HF equations have the form:

$$\hat{f}\varphi_a(r_1) = \epsilon_a\varphi_a(r_1) \qquad (1.15)$$

$$\hat{f} = \hat{h} + \sum_{b=1}^{N/2}\hat{J}_b - \hat{K}_b \qquad (1.16)$$

where $\hat{f}$ is the closed-shell Fock operator, ϵ_a is the orbital energy, $\hat{h}$ is the one electron part of the Hamiltonian, $\hat{J}_b$ and $\hat{K}_b$ are the Coulomb and exchange operators, respectively:[3]

$$J_b\varphi_a(r_1) = \int\left[\varphi_b^*(r_2)\frac{1}{r_{12}}\varphi_b(r_2)dr_2\right]\varphi_a(r_1) \qquad (1.17a)$$

$$K_b\varphi_a(r_1) = \int\left[\varphi_b^*(r_2)\frac{1}{r_{12}}\varphi_a(r_2)dr_2\right]\varphi_a(r_1) \qquad (1.17b)$$

Spatial functions can be expanded in a finite basis set $\{\psi_s\}_{s=1}^{k}$:[3,4]

$$\varphi_i = \sum_{\mu=1}^{b} c_{\mu i}\psi_\mu \qquad (1.18)$$

where the choice of the size of the basis is dictated by the degree of expected accuracy and computational cost, while the condition of orthogonality is always imposed on the basis, as the resulting HF equations are easier to solve.[12]

Substitution of the basis set expansion in equation (1.18) into the Hartree-Fock equations (1.16) leads to the Roothaan's equations that can be written as a set of *b* equations in the variables $c_{\mu a}$ (eq. 1.19)[12] or in a matrix form (eq. 1.20)[3,4] as:

$$\sum_{\mu=1}^{b} c_{\mu a}\left(F_{\mu\nu} - \epsilon_a S_{\mu\nu}\right) = 0 \tag{1.19}$$

$$\boldsymbol{FC} = \boldsymbol{SC\epsilon} \tag{1.20}$$

where $\boldsymbol{F}$ is the Fock matrix with the matrix elements $F_{\mu\nu} = \langle\psi_\mu|\hat{f}|\psi_\nu\rangle$; $\boldsymbol{S}$ is the overlap matrix with the matrix elements $S_{\mu\nu} = \langle\psi_\mu|\psi_\nu\rangle$, **C** is the expansion coefficients matrix, and $\boldsymbol{\epsilon}$ is the diagonal matrix of orbital energies.

$$\boldsymbol{C} = \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1k} \\ c_{21} & c_{22} & \cdots & c_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ c_{k1} & c_{k2} & \cdots & c_{kk} \end{pmatrix} \qquad \boldsymbol{\epsilon} = \begin{pmatrix} \epsilon_{11} & 0 & \cdots & 0 \\ 0 & \epsilon_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \epsilon_{kk} \end{pmatrix} \tag{1.21}$$

The Fock operator is dependent on the molecular orbital coefficients through the Coulomb and exchange operators; therefore, an initial guess or prior knowledge of the coefficient matrix is required to solve Roothaan's equations. Thus, the pseudo-eigenvalue Hartree-Fock equations are nonlinear equations, solved by the iterative procedures.

The probability of finding an electron described by the spatial wavefunction φ_a, in the volume $d\boldsymbol{r}$ at a point $\boldsymbol{r}$ is $|\varphi_a(\boldsymbol{r})|^2 d\boldsymbol{r}$. The probability distribution function, charge density, is $|\varphi_a(\boldsymbol{r})|^2$. The total charge density of a system described by the closed-shell single determinantal wavefunction is a sum of the charge densities of all occupied molecular orbitals, and the integral of the total charge density is simply the total number of electrons.[3]

$$\rho(\boldsymbol{r}) = 2\sum_{a}^{N/2} |\varphi_a(\boldsymbol{r})|^2 \tag{1.22}$$

$$\int \rho(\boldsymbol{r})\, d\boldsymbol{r} = 2\sum_{a}^{N/2} \int |\varphi_a(\boldsymbol{r})|^2\, d\boldsymbol{r} = 2\sum_{a}^{N/2} 1 = N \tag{1.23}$$

Defining the density matrix **P** as: **P**=2**CC**$^{+}$ with matrix elements $P_{\mu\nu} = 2\sum_{a=1}^{N/2} C_{\mu a} C_{\nu a}^{*}$, the electron density term can be written in terms of $P_{\mu\nu}$.

$$\rho(\boldsymbol{r}) = 2\sum_{a}^{N/2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_{\mu a}^{*} C_{\nu a} \psi_{\mu}^{*}(\boldsymbol{r})\psi_{\nu}(\boldsymbol{r}) = \sum_{\mu\nu} P_{\nu\mu}\psi_{\mu}^{*}(\boldsymbol{r})\psi_{\nu}(\boldsymbol{r}) \tag{1.24}$$

The charge density matrix specifies completely the charge density in terms of the expansion coefficients, and the closed-shell Fock operator can be expressed in terms of the density matrix[3]

$$\hat{f}(\boldsymbol{r}_1) = \hat{h}(\boldsymbol{r}_1) + \sum_{b=1}^{\frac{N}{2}} \hat{J}_b - \hat{K}_b = \hat{h}(\boldsymbol{r}_1) + v^{HF}(\boldsymbol{r}_1)$$

$$= \hat{h}(\boldsymbol{r}_1) + \frac{1}{2}\sum_{\nu\mu} P_{\nu\mu}\left[\int \psi_{\mu}^{*}(\boldsymbol{r}_2)(2 - \mathcal{P}_{12})\frac{1}{\boldsymbol{r}_{12}}\psi_{\nu}(\boldsymbol{r}_2)d\boldsymbol{r}_2\right] \tag{1.25}$$

where the $v^{HF}$is an effective one-electron potential, and the $\mathcal{P}_{12}$ is the permutation operator, which permutes the coordinates of the particles. The most commonly used approach to find the solutions to the Roothaan's equations is the self-consistent field (SCF) approach. The SCF approach most often uses the charge density matrix for the convergence test; the initial guess of the molecular orbitals determines the initial density matrix, which is used to calculate the effective one-electron Hartree-Fock potential, and therefore a new charge density. The SCF procedure is repeated until an effective electrostatic field no longer changes; therefore, until the field that produced a particular charge density is consistent with the field calculated from that same charge density.[3]

The above restricted closed-shell Hartree-Fock equations using the pairs of electrons in the closed shells are of course not sufficient to describe all molecules nor all their states; the restricted and unrestricted open-shell calculations were developed to deal with many of these electronic structure problems in chemistry. In the restricted open-shell Hartree-Fock procedure, all electrons, except for those that are required to occupy open-shell orbitals, are placed in closed-shell orbitals. The wavefunctions obtained in this way are the eigenfunctions of the spin operator; however, the constraint of occupying the orbitals in pairs raises the energy compared to the energy obtained using the unrestricted open-shell calculations. The unrestricted Hartree-Fock equations are derived in the similar way as the restricted Roothaan's equations, by minimizing the total energy of the system; although, the spin orbitals need to be inserted into the equations and integrated over. Therefore, α and β spin electrons are described by different sets of spatial orbitals, and their energy will also differ.[3] The unrestricted Hartree-Fock equations, the Pople-Nesbet equations, contain two (α and β) Fock operators, and the corresponding Coulomb and exchange operators are defined in similar way as for the Roothaan's equations. The result is two sets of integro-differential eigenvalue equations that are coupled through the coulomb and exchange integrals, and need to be solved simultaneously by an iterative process.

The Hartree-Fock approximation is remarkably successful in many computational chemistry problems; however, it also has many limitations. A single determinantal wavefunction cannot correctly describe many of the molecular or atomic systems and their states; however, it is often accurate and efficient in predicting correct molecular

structure. Although the Hartree-Fock energy accounts for roughly 99% of the total electronic energy, it ignores the correlation between electrons, which is extremely important, especially for the cases that involve bond breaking and forming.

1.4. Post Hartree-Fock Wavefunction Methods

Many of the methods developed to account for the missing electron correlation, such as configuration interaction (CI) theory, the coupled-cluster (CC) approximation, multiconfiguration SCF (MCSCF), and Møller-Plesset (MP) perturbation theory are based on the Hartree-Fock theory.[3] Post Hartree-Fock methods are however computationally costly, and are in general not practical for larder molecular systems, sometimes even for those containing two monomers.

The variational CI theory uses a multi-determinantal wavefunction, which is a linear combination of Slater determinants that correspond to different electronic configurations of the system.[3,6]

$$|\Psi_{CI}\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r\,|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\,|\Psi_{ab}^{rs}\rangle + \cdots \qquad (1.26)$$

The full CI matrix is the Hamiltonian matrix in the basis of all possible *N*-electron functions formed by replacing *N* spin orbitals in Hartree-Fock wavefunction, Ψ_0. Singly excited CI refers to a form of a CI trial wavefunction which contains determinants that differ from Ψ_0 by one spin orbital, $|\Psi_a^r\rangle$, doubly excited CI wavefunction contains determinants that differ from Ψ_0 by two spin orbitals, $|\Psi_{ab}^{rs}\rangle$, and so forth. In practice, the full CI is always truncated in some form, formed by a combination of singly, doubly,

triply, etc. excited determinants multiplied by the CI expansion coefficients. The CI problem can be written as an eigenvalue equation.[3]

$$\boldsymbol{Hc} = \boldsymbol{Ec} \tag{1.27}$$

where $\boldsymbol{E}$ is a diagonal matrix of energies, $\boldsymbol{c}$ is the CI coefficient vector, and $\boldsymbol{H}$ is the CI matrix, with the elements H_{IJ}.

$$H_{IJ} = \langle \Psi_I | \hat{H} | \Psi_J \rangle \tag{1.28}$$

The solution is obtained by the determination of the optimal expansion coefficients set. The CI method uses the canonical Hartree-Fock orbitals, which are in general not the best choice for truncated CI calculations. To obtain the best possible approximation to an exact solution, the orbitals should also vary so as to minimize the energy, which is the multiconfiguration self-consistent field method (MCSCF).[3]

$$|\Psi_{MCSCF}\rangle = \sum_I c_I \, |\Psi_I\rangle \tag{1.29}$$

The MCSCF wavefunction is a truncated CI expansion, in which both the expansion coefficients and the orthonormal orbitals are optimized. In the limits of a complete basis set (complete CI), and in the limit of all possible determinants applicable to a particular system (full CI), the non-relativistic CI wavefunction would approach the exact; the CI energies of the ground state, and also the CI energies of the excited states would approach the exact values. Therefore, CI provides a method to obtain an exact solution to the many-electron problem; in practice however, it is not possible to handle the infinite set of basis functions. Because the CI method is variational, it does provide the upper bound to the exact electronic energy; however, truncated CI; although it is

variational, is not size consistent: the truncated CI energy of non-interacting molecules is not equal to a sum of their individual CI energies.

An alternative method to truncated CI is the coupled-cluster approximation; however, the CC approximation is very computationally expensive and although it is size consistent, it is not variational. The CC wavefunction is constructed as a cluster expansion of the Hartree-Fock wavefunction, and contains double, quadruple, hextuple, etc. excitations such that the coefficients of the $2n^{\text{th}}$-tuple excitations are approximated by products of n doubly excited coefficients.[3]

$$|\Psi_{CC}\rangle = e^{\hat{\mathcal{T}}}|\Psi_0\rangle \tag{1.30}$$

where the cluster operator, $\hat{\mathcal{T}}$ is a sum of operators $\hat{\mathcal{T}}_i$, which produce excited determinants from the Hartree-Fock wavefunction.

$$\hat{\mathcal{T}} = \sum_{i=1}^{N} \hat{\mathcal{T}}_i \tag{1.31}$$

The exponential cluster operator can be expanded as a Taylor series, and the approximations are based on the truncated expansion.

$$e^{\hat{\mathcal{T}}} = 1 + \hat{\mathcal{T}} + \frac{\hat{\mathcal{T}}^2}{2!} + \cdots \tag{1.32}$$

The most common form of CC is CCSD(T), where the cluster expansion of the wavefunction is truncated at the doubles operator, while the triple excitations are approximated, rather than including a triples operator. The quadruple excitations in CCSD are approximated as a product of double excitations.

Probably the most often used post Hartree-Fock wavefunction method is the Møller-Plesset (MP) perturbation theory. MP is based on Rayleigh-Schrödinger

perturbation theory. The correction to the zeroth-order Hamiltonian, $\hat{H}_0$, which has known eigenfunctions and eigenvalues is added as a perturbation, $\hat{\mathcal{V}}$, to give the perturbed Hamiltonian, $\hat{H}$.[4]

$$\hat{H} = \hat{H}_0 + \hat{\mathcal{V}} \tag{1.33}$$

where the perturbation is expressed as:

$$\hat{\mathcal{V}} = \sum_{i=1}^{N} \sum_{j<i} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \hat{\mathcal{V}}_{HF}(i) \tag{1.34}$$

and $\hat{\mathcal{V}}_{HF}(i)$ the is the effective Hartree-Fock potential.

$$\hat{\mathcal{V}}_{HF}(i) = \sum_{j=1}^{N} \left(\hat{J}_j(i) - \hat{K}_j(i) \right) \tag{1.35}$$

The exact eigenfunctions and eigenvalues can be expanded in a Taylor series in λ as:

$$|\Phi_i\rangle = \left|\Psi_i^{(0)}\right\rangle + \lambda \left|\Psi_i^{(1)}\right\rangle + \lambda^2 \left|\Psi_i^{(2)}\right\rangle + \cdots \tag{1.36}$$

$$\mathcal{E}_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots \tag{1.37}$$

The zeroth-order MP energy is the sum of HF orbital energies, while the total HF energy is given by the sum of zeroth-order and first-order MP energies.[3] The first correction to the HF energy is given by second-order MP energy. As the order in MP theory increases, the correction terms get more complex and more complicated to calculate. The MP_n theory is size consistent, but not variational; therefore, it is possible for the calculated energy of $(n)^{th}$-order to be lower than the energy of $(n+1)^{th}$-order, or even lower than the exact non-relativistic energy.

1.5. Valence Bond Theory

Valence bond (VB) theory remains a conceptually essential part of basic chemical theories as it offers many interesting and novel insights into the nature of chemical bond. The VB method, which appeared as a quantum mechanical formulation of Lewis's electron-pair bonding model,[13] became attractive from the chemist's point of view; however, the accurate mathematical treatment of the VB approach was computationally very cumbersome. One of the issues causing the substantial computational demand of the VB method is the exponential increase in the number of determinants used in linear combination to write the VB wavefunction, which scales as 2^n, where n is the number of covalent bonds in the corresponding VB structure. The second, more challenging computational problem arises from the non-orthogonal treatment required by VB theory, in sharp contrast to the orthogonality of the molecular orbitals used in Molecular Orbital (MO) theory.[14] However, since the 1980s the number of VB theory based quantitative applications is growing, mainly due to the exponential increase of the computational power, numerous modern methodological contributions and the appearance of new VB methods and implementations. The VB theory is gaining popularity today.

The increased popularity of MO theory does not necessary imply that one theory is better than the other; a properly executed VB method converges to the same result as a properly executed MO method. While the simple VB wavefunction is a linear combination of antisymmetrized products of AOs, the MO wavefunction in its Hartree-Fock (HF) approximation is constructed as a linear combination of atomic orbitals (LCAO).[14]

The traditional Heitler and London (HL) wavefunction, Φ_{HL}, describes a two-electron bond as being purely covalent:[15]

$$\Phi_{HL} = |a\bar{b}| - |\bar{a}b| \tag{1.38}$$

where a and b are respective AOs of two bonded atoms, ignoring the normalization constant. One of the virtues of VB description is that it correctly describes the dissociation of a covalent bond, but it is quantitatively inaccurate at bonding distances. On the other hand, a simple MO wavefunction describes a two-electron bond using molecular orbitals: doubly occupied bonding MO, $\sigma = a + b$, and a virtual antibonding MO, $\sigma^* = a - b$. The expansion of MO determinant into its AO constituents (ignoring the normalization constant) leads to Ψ_{MO}.

$$\Psi_{MO} = |\sigma\,\bar{\sigma}| = \left(|a\bar{b}| - |\bar{a}b|\right) + \left(|a\bar{a}| + |b\bar{b}|\right) \tag{1.39}$$

Therefore, in MO description, the homopolar two-electron bond will have half-ionic and half-covalent character irrespective of the bonding distance, and although it gives reasonably accurate results at the equilibrium bonding distance, the MO approach is incorrect at the dissociation limit.[14]

The accurate description of a two-electron bond, which is mostly covalent, but has some contribution from the ionic structures is between simple VB and simple MO approaches. The improvement to the VB HL wavefunction can be done by mixing the simple Φ_{HL} with the ionic determinants, and optimizing the coefficients (λ and μ) variationally in order to obtain $\Psi_{VB\text{-}full}$.

$$\Psi_{VB-full} = \lambda\left(|a\bar{b}| - |\bar{a}b|\right) + \mu\left(|a\bar{a}| + |b\bar{b}|\right) \tag{1.40}$$

Similarly, the simple MO description is improved by configuration interaction (CI), mainly by mixing of the ground state configuration with the doubly excited one, Ψ_D.

$$\Psi_D = |\sigma^* \bar{\sigma}^*| = -\left(\left|a\bar{b}\right| - |\bar{a}b|\right) + \left(|a\bar{a}| + \left|b\bar{b}\right|\right) \quad (1.41)$$

Mixing the two configurations, Ψ_{MO} and Ψ_D, with different coefficients (c_1, c_2) that are optimized variationally leads to $\Psi_{MO\text{-}CI}$ wavefunction.

$$\Psi_{MO-CI} = c_1|\sigma\,\bar{\sigma}| - c_2|\sigma^*\,\bar{\sigma}^*| \qquad c_1, c_2 > 0 \quad (1.42)$$

Expanding $\Psi_{MO\text{-}CI}$, in which the covalent and ionic components have different weights, into AO determinants gives the wavefunction as:

$$\Psi_{MO-CI} = (c_1 + c_2)\left(\left|a\bar{b}\right| - |\bar{a}b|\right) + (c_1 - c_2)\left(|a\bar{a}| - \left|b\bar{b}\right|\right) \quad (1.43)$$

which is equivalent to $\Psi_{VB\text{-}full}$, since all coefficients are optimized variationally in both improved VB and MO methods, which gives $(c_1 + c_2) = \lambda$ and $(c_1 - c_2) = \mu$.[14] Therefore, both theories converge to the correct description when CI is introduced to MO, and are two mathematically equivalent representations of a two-electron bond. There is a wide range of orbital representations between fully localized VB and fully delocalized MO descriptions, and it is likely that the best representation of a covalent bond is by taking advantage of VB theory and MO theory complementarity.

1.6. Density Functional Theory

Although in most cases the post Hartree-Fock wavefunction methods are very successful in improving the accuracy of the HF results for quantum chemistry calculations, one common drawback they all share is their computational cost. The computational costs of the post HF methods increases considerably with the number of

basis functions used in the calculations, and even with today's computational resources, they cannot be used to study large molecular systems. The alternative method to the wavefunction approach is density functional theory (DFT). In DFT, the energy is expressed as a functional of the electron density, ρ(**r**).[16]

$$E[\rho(\boldsymbol{r})] = T_e[\rho(\boldsymbol{r})] + V_{ne}[\rho(\boldsymbol{r})] + V_{ee}[\rho(\boldsymbol{r})] + \Delta T[\rho(\boldsymbol{r})] + \Delta V_{ee}[\rho(\boldsymbol{r})] \qquad (1.44)$$

The $\Delta T[\rho(\boldsymbol{r})]$ term is a correction to the kinetic energy of the electrons, $T_e[\rho(\boldsymbol{r})]$, while the $\Delta V_{ee}[\rho(\boldsymbol{r})]$ term contains all the non-classical corrections to the electron-electron repulsion energy, $V_{ee}[\rho(\boldsymbol{r})]$, and the $V_{ne}[\rho(\boldsymbol{r})]$ is the classical nucleus-electron potential energy.

$$V_{ne}[\rho(\boldsymbol{r})] = \sum_{A}^{nuclei} \int \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{r_A}|} \rho(\boldsymbol{r}) d\boldsymbol{r} \qquad 1.45)$$

$$V_{ee}[\rho(\boldsymbol{r})] = \frac{1}{2} \iint \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \qquad (1.46)$$

These corrections are defined together as the exchange-correlation energy, $E_{xc}[\rho(\boldsymbol{r})]$.[16]

$$\Delta T[\rho(\boldsymbol{r})] + \Delta V_{ee}[\rho(\boldsymbol{r})] = E_{xc}[\rho(\boldsymbol{r})] = \int \rho(\boldsymbol{r}) \epsilon_{xc}[\rho(\boldsymbol{r})] d\boldsymbol{r} \qquad (1.47)$$

The DFT energy functional is minimized using Kohn-Sham (KS) equations, which define the system of non-interacting electrons and their corresponding Kohn-Sham orbitals, $\{\varphi_i^{KS}\}$, described by a Slater determinant:

$$\hat{h}_i^{KS} \varphi_i^{KS} = \epsilon_i^{KS} \varphi_i^{KS} \qquad (1.48)$$

where the ground state electron density can be written as:

$$\rho_0(\boldsymbol{r}) = \rho^{KS}(\boldsymbol{r}) = \sum_{i=1}^{N} \varphi_i^{KS*}(\boldsymbol{r}) \varphi_i^{KS}(\boldsymbol{r}) \qquad (1.49)$$

and the KS one-electron operator $\hat{h}_i^{KS}$ is:

$$\hat{h}_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum \frac{Z_A}{\boldsymbol{r}_{iA}} + \int \frac{\rho(\boldsymbol{r}_2)}{\boldsymbol{r}_{i2}} d\boldsymbol{r}_2 + \hat{v}_{xc}(\boldsymbol{r}_i) \tag{1.50}$$

where $\hat{v}_{xc}(\boldsymbol{r})$ is the exchange-correlation operator, defined as the functional derivative of the exchange-correlation energy with respect to the density.[16]

$$\hat{v}_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}[\rho(\boldsymbol{r})]}{\delta \rho(\boldsymbol{r})} \tag{1.51}$$

The exact form of the exchange-correlation functional operator is unknown; however, it is reasonable to approximate the exchange-correlation functional operator as a sum of the exchange, $\hat{v}_x(\boldsymbol{r})$, and correlation, $\hat{v}_c(\boldsymbol{r})$, operators.[16]

$$\hat{v}_{xc}(\boldsymbol{r}) = \hat{v}_x(\boldsymbol{r}) + \hat{v}_c(\boldsymbol{r}) \tag{1.52}$$

Like HF equations, the KS equations are solved iteratively using SCF method. While the kinetic energy, electron-nuclear potential energy, and Coulomb electron-electron potential are calculated as integrals over the basis functions, similar to HF theory, the exchange-correlation integrals are often too complex to be expressed analytically; therefore, the exchange-correlation energy is calculated using numerical integration. Because the exact form of the exchange-correlation operator is unknown, the DFT method employs approximate exchange-correlation operator. Therefore, even though the general form of DFT is variational, the approximate form of DFT is not. Several forms of exchange-correlation operators have been developed and are used today in many applications, some more popular than others, but in general, it is often necessary to select the most suitable functional depending on the system studied and the properties of interest.

2. Electron Correlation

2.1. Introduction

2.1.1. Electron Correlation

In HF theory, the Pauli principle is obeyed within the antisymmetric HF wavefunction, and it assures that the correlation of electrons with parallel spin is accounted for by the exchange interaction;[17] however, in the HF single-determinantal wavefunction theory, the motion of electrons with opposite spin is completely neglected, and the probability of finding two electrons with opposite spin at the same point in space is not equal to zero. The difference between the exact non-relativistic energy and the HF energy, using a complete basis set is defined as the correlation energy:[18]

$$E_{corr} = \mathcal{E}_0 - E_{HF_{limit}} \tag{2.1}$$

The error caused by the neglect of the correlation energy in light atoms is less than 1% of the total electronic energy. However, the error is larger for even the smallest molecular systems, and can lead to incorrect thermodynamics and kinetics results, especially for the reaction systems where the correlation energy does not remain constant with respect to the reactants' and products' correlation energies.[19-22] It is a very important and challenging goal to account for the missing correlation energy in purely *ab initio* calculations. This requires highly accurate and computationally very expensive post Hartree-Fock methods; therefore, many of the computationally accessible empirical methods, such as B3LYP density functional method or the Gaussian-n methods, are parameterized to reproduce accurate thermochemical data.[22] The efficient calculation of

the Coulomb interaction and an accurate description of what happens when two electrons come close together remains one of the most active research topics in modern computational chemistry, almost a century after the formulation of quantum mechanics.[2]

2.1.2. Fermi and Coulomb Correlation

The nature of the correlation in the electronic wavefunctions has two independent forms: Fermi correlation and Coulomb correlation.[23] Fermi correlation arises from the fact that the electrons are countable but indistinguishable, and obey Fermi statistics. Fermi statistics requires that the wavefunction is antisymmetric with respect to the exchange of configurations $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ for any pair of electrons, where $\boldsymbol{x}$ is a composite of space and spin coordinates: $\boldsymbol{x}=(r_x,r_y,r_z,\omega)$.[23] The first consequence of the above is that any expansion of the wavefunction has zero contribution from the *n*-electron orbital product wavefunctions where two or more electrons occupy the same spin orbital; hence, the probability of finding two electrons with parallel spin at the same point in space is zero. This statistical correlation has by far the largest contribution to the correlation energy between electrons, and it is included in the Hartree product wavefunction as long as the electron indistinguishability is taken into account. The second consequence of Fermi correlation introduces additional (exchange) correlation, through the wavefunction antisymmetry requirement.[23] While the $\boldsymbol{x}$ composite coordinate includes both space and spin coordinates, the non-relativistic Hamiltonian is spin free; therefore, the applicable spatial probability distribution can be obtained by integrating over the spin coordinates in $\rho(\boldsymbol{x})$ and $\rho_{12}(\mathbf{x}_1,\mathbf{x}_2)$ to give $\rho(\boldsymbol{r})$ and $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$. The exchange correlation lowers the probability of the same spin electrons being close in space (called

the exchange hole), and it goes over and above the statistical correlation of the two like-spin electrons being at the same point.[23] Fermi correlation is completely unrelated to the repulsive electrostatic interaction between the electrons; rather, it is a fundamental consequence of their quantum nature.[2]

The Fermi correlation is contained in the Hartree-Fock wavefunction; therefore, Löwdin's definition of the correlation energy based on a restricted HF wavefunction refers to the missing Coulomb correlation only. Hartree-Fock theory is a mean-field theory: the repulsion between the electrons only affects the wavefunction through the effective potential; however, motion of an electron depends on the instantaneous interactions with all the other electrons.[23] This missing electron correlation is the Coulomb correlation, and it is usually negative for the ground-state of a system as it tends to reduce the probability of finding two electrons in the same region of space. The source of the Coulomb correlation arises from the instantaneous electrons' interaction through the repulsive electrostatic Coulomb force, and it is inversely proportional to the distance between the electrons, r_{12}.

$$F_c = \frac{q_e^2}{4\pi\varepsilon_0 r_{12}} \tag{2.2}$$

For very small atomic systems the Coulomb correlation is a relatively small perturbation of the Hartree-Fock energy, and it arises purely from the instantaneous electron-electron repulsion, sometimes referred to as a dynamic Coulomb correlation. However, there are numerous cases where a single Hartree-Fock configuration, a single Hartree-Fock determinant, is not sufficient to properly describe a system, and at least two configurations are necessary, especially when considering homolytic bond

cleavage. The Coulomb correlation in this case is referred to as a non-dynamical, or static correlation.[23]

2.1.3. Dynamic and Static Correlation

The Coulombic interactions (as well as the energetic effects of Fermi correlation) depend strongly on the internuclear separation. At the short separation, the electron correlation is discussed in terms of short-range effects of the dynamic correlation. Dynamic Coulomb correlation arises from the inability of the Hartree-Fock wavefunction to properly describe the instantaneous interactions between electrons when they come close to one another.[24] At large separation, the electron correlation is often thought in terms of long-range effects of a non-dynamic, static correlation. Static Coulomb correlation is a result of the inability of the Hartree-Fock wavefunction to accurately describe the electronic configuration of a system due to near degeneracies, and corresponds to the tendency of the electrons to be associated with certain regions of space.[24] However, strict distinction between static and dynamic correlation is not possible in general.

When visualizing the electron correlation in molecules it is often common to consider three separate kinds of electron correlation descriptors: radial, angular, and left-right correlation. These are not necessary specific to either Fermi or Coulomb correlation. The radial, or *in-out*, correlation refers to a case when an electron is close to a nucleus, and it is more probable to find all the other electrons far out from that nucleus. The radial correlation improves the description of the interaction between the electrons by using additional electronic configurations that include atomic orbitals of the same

angular quantum number but higher principal quantum number, for example, using 2s and 3s orbitals to describe He($1s^2$).[24] The angular correlation refers to a case when an electron is on one side of a nucleus, and it is more probable to find all the other electrons on the other side of that nucleus. Angular correlation furthers the correction to the electron correlation through the added configurations of higher angular quantum numbers.[24] Radial and angular correlations are separable when using a nucleus as the origin, and are useful in the electron correlation description in atoms or close to each nucleus in molecules.[23] Left-right correlation implies the tendency of the electrons to move towards different nuclei, such as if an electron is close to a nucleus on the left side of a chemical bond it is more probable for the other electrons to be close to the nucleus on the right side.[23] Left-right correlation is useful to describe correlation between electrons in the regions between the atoms in a molecule. For example in the triplet state of the hydrogen molecule there is a Fermi hole around the Fermi node, and if an electron is close to one nucleus, the other electron is likely found close to the other nucleus (strong negative left-right correlation). On the other hand, in the singlet state of the hydrogen molecule there is a Fermi heap around the Fermi hole resulting from the strong positive left-right correlation, and it is more probable to find two electrons on the same nucleus than on the different nuclei.[23] Some other useful partitioning for the electron correlation have also been proposed. For example Clementi[25] suggested division of the electron correlation into atomic, covalent, ionic, and van der Waals contributions, which can be useful in the analysis of the electron correlation in different systems and help in the development of new approaches.[24]

2.2. Existing Models for the Correlation Energy

2.2.1. The Expansion of the Correlation Energy in Z^{-1}

For small atomic systems it is possible to obtain near exact correlated wavefunction. The first successful electronic structure computation of an explicitly correlated wavefunction was determined for the helium atom ground state by Hylleraas.[26] In the Hylleraas expansion, the spatial part of the He ground state wavefunction assumes the form:[26]

$$\Psi_N = exp(-\xi(r_1 + r_2)) \sum_{k=1}^{N} c_k (r_1 + r_2)^{l_k} (r_1 - r_2)^{2m_k} r_{12}^{n_k} \tag{2.3}$$

where r_1 and r_2 are the distances of the first and second electron from the nucleus, respectively, and r_{12} is the inter-electronic distance. Although Hylleraas obtained very accurate electronic energy after variationally optimizing the linear and non-linear parameters, the techniques used for the helium atom become extremely complex when applied to larger systems and are not useful in practical applications. Hylleraas also expressed the exact energy of the helium-like ion as a Laurent series of the nuclear charge Z using perturbation theory.[27] Davidson and co-workers estimated the expansion of the exact non-relativistic energy, Hartree-Fock energy, and correlation energy for isoelectronic series of 2 to 18 electrons using experimental and *ab initio* values:[28,29]

$$E_{exact}(N,Z) = B_0(N)Z^2 + B_1(N)Z + B_2(N) + B_3(N)Z^{-1} + \cdots \tag{2.4}$$

$$E_{HF}(N,Z) = B_0^{HF}(N)Z^2 + B_1^{HF}(N)Z + B_2^{HF}(N) + B_3^{HF}(N)Z^{-1} + \cdots \tag{2.5}$$

$$E_{corr}(N,Z) = \Delta B_0(N)Z^2 + \Delta B_1(N)Z + \Delta B_2(N) + \Delta B_3(N)Z^{-1} + \cdots \tag{2.6}$$

where each N dependent coefficient in the correlation expansion series is given by $\Delta B_i(N)$.

$$\Delta B_i(N) = B_i(N) - B_i^{HF}(N) \tag{2.7}$$

In cases where a single configuration with hydrogenic orbitals is a reasonably accurate approximation to the exact wavefunction, the two leading coefficients in the expansion of the exact and the Hartree-Fock energy are equivalent,[29] and therefore the quadratic and linear terms in Z do not appear in the correlation energy expansion. For the isoelectronic series with N = 4, 5, 6, and N >12 a single configuration is not a satisfactory approximation; therefore, the linear coefficients for the exact and Hartree-Fock energies are not equal.[29] In these cases, the correlation energy expansion begins with a residual linear term in Z. The correlation energy as a function of Z for the isoelectronic series for N=2-18,[28,29] and as a function of N for each atomic number series is given in Figure 2.1 and in Figure 2.2, respectively.

2.2.2. The Size of an Electron Pair

Some of the earlier attempts at modelling of the electron correlation in atomic systems explored the inverse relationship between the correlation energy and some measure of size. It has been shown that the correlation energies of different structural isomers change in relation to the volume available to the electrons, even though there is no change in the nuclear charges within the molecules.[30] It is reasonable to assume that the correlation between the electrons should increase as the volume occupied by an electron pair decreases; in other words, the closer the electrons are to each other, the more correlated their motion.

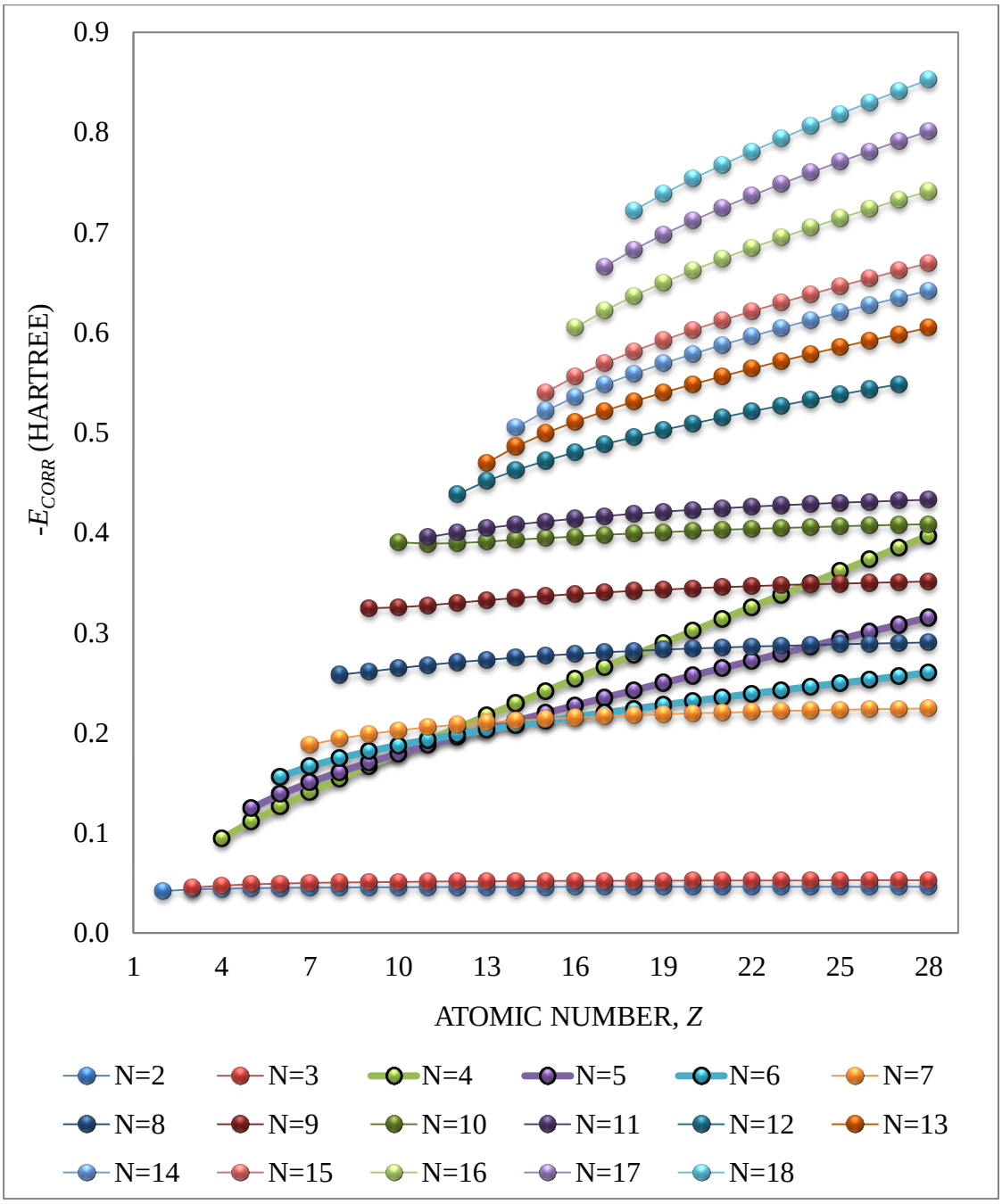


Figure 2.1. Correlation energy as a function of nuclear charge, Z for the isoelectronic atomic series of N=2-18**.**

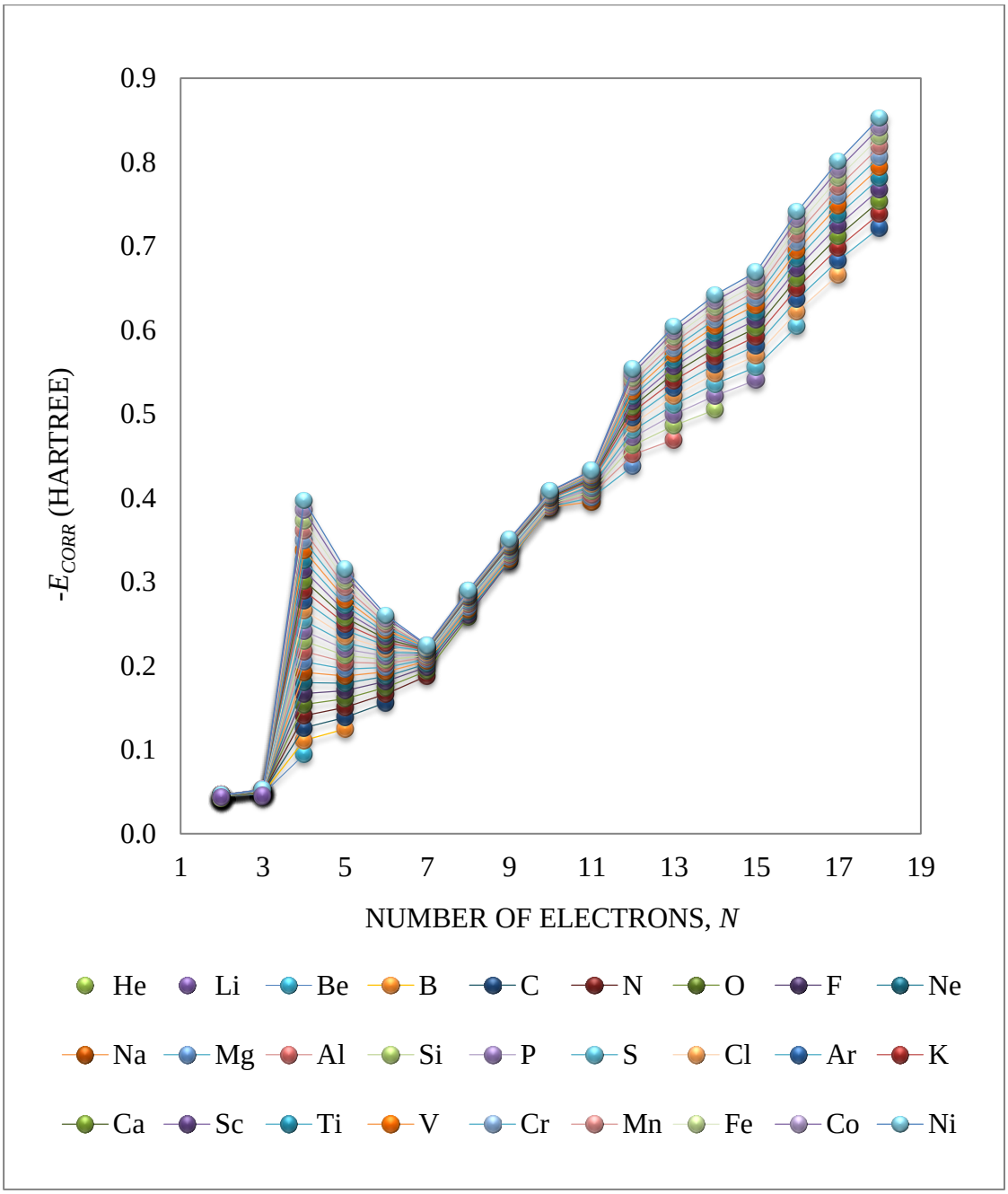


Figure 2.2. Correlation energy as a function of number of electrons, N for the isoelectronic atomic series of N=2-18.

Fröman proposed a semi-empirical formula using the mean value of the inter-electronic distance of the form:[17]

$$E_{corr} = \frac{1}{aZ + b}\langle\frac{1}{r_{12}}\rangle_{Ave,HF} \tag{2.8}$$

where *a* and *b* were determined to be -0.520, and -0.167, respectively for helium-like systems using atomic units for the parameter $\langle 1/r_{12}\rangle_{Ave,HF}$.[17] Bernardi *et. al.*[31] defined the size of an electron pair for the helium-like atoms as an expectation value of the spherical quadratic operator, r^2; the volume of an i^{th} atomic orbital can be then calculated from its size.[32]

$$V_i = \frac{4\pi}{3}\ \langle r_i^2\rangle^{\frac{3}{2}} \tag{2.9}$$

An inverse relationship between the correlation energy and the size of an electron pair was suggested as:[33-35]

$$E_{corr} = \frac{K}{(Z-\sigma)^{\gamma}\langle r^2\rangle} \tag{2.10}$$

in which σ is a screening constant, the parameter $K = -0.276698$, $\gamma = 2$ for the helium-like ions, and $\langle r^2\rangle$ is a second moment of the electron density. Their results indicated that the total size as weighted by the effective nuclear charge appears to be the most important factor in the approximation of the correlation energies for isoelectronic ions. They also note that Fröman's relation in equation (2.8) can be rewritten in a form similar to equation (2.10).[31]

$$E_{corr} = \frac{-0.070702}{(Z-0.32115)}\langle\frac{1}{r_{12}}\rangle_{Ave,HF} \tag{2.11}$$

López-Boada *et. al.* derived inequality relationship between the correlation energy and the expectation value of r^2 based on the gradient expansion approximation:

$$E_{corr} \leq \frac{F(N,Z)}{\langle r^2 \rangle} \tag{2.12}$$

in which *F* is an unknown function of *N* and *Z*.[36] Bernardi *et. al.*[31] also showed that the size of an electron pair and the volume occupied by a pair is *Z* dependent, and therefore, the dependence of the correlation energy on the size might arise naturally from its dependence on atomic number, *Z*. It might be possible that we only need to parameterize one of these variables in the electron correlation modelling. However, the size of an electron pair alone cannot account for the total correlation energy, and other parameters should be included.

Models describing the relationships between the correlation energy and size of the electron pair in the atomic series have been extended and applied to the molecular systems. Modelling of the electron correlation in molecules showed that the crude amount of the missing energy could be accounted for from the size of an electron pair.[37,38] The size of an electron pair associated with a localized molecular orbital (LMO), $\langle r^2 \rangle_{R_a}$ is defined as:[35]

$$\langle r^2 \rangle_{R_a} = \langle \psi_a | r^2 | \psi_a \rangle_0 - R_a^2 \tag{2.13}$$

where R_a is the centroid of charge of the LMO calculated at a point R_0.[34]

$$R_a^2 = \langle \psi_a | x_1 | \psi_a \rangle_0^2 + \langle \psi_a | y_1 | \psi_a \rangle_0^2 + \langle \psi_a | z_1 | \psi_a \rangle_0^2 \tag{2.14}$$

The size of a localized molecular orbital *a* has been related to the orbital energy, ϵ_a,[32]

$$\left(\frac{1}{\epsilon_a}\right) = m\langle r^2 \rangle_a + b \tag{2.15}$$

where *m* and *b* are fitting parameters. The simple model relating atomic correlation energy to size in eq. (2.10) has been later extended to the molecular systems relating the molecular correlation energy to the LMO size.[38]

$$E_{corr} = C \sum_{i=1}^{M} \frac{1}{\langle r^2 \rangle_i} \tag{2.16}$$

$$E_{corr} = -0.06593 \sum_{i=1}^{M} \langle r^2 \rangle_i^{-0.1958} \tag{2.17}$$

The mean error obtained using the above model and STO-3G basis set calculations for a group of molecules and atoms in their study is comparable to that of some of the density functional methods,[38] which suggests that these simple molecular correlation size models might be quite useful and applicable in the wide range of theoretical chemistry studies due to their computational efficiency.

López-Boada *et. al.* used Bader's[39] approach of partitioning a molecule into the subsystems by means of zero flux surfaces, and extended atomic correlation models to the molecular systems by computing the correlation energy of each fragment using the relationship between the correlation energy and the expectation value of r^2 in eq. (2.12).[36] Their results are fairly good, considering the simplicity of the approximation; however, it has become obvious than the size alone cannot account for the total correlation energy, and other parameters should be included to derive more accurate correlation models.

2.2.3. Atomic Number and the Number of Electrons Models

Although the correlation energy of neutral atoms in their ground state shows approximately linear dependence on the number of electrons, *N*, the deviation from this linearity appears for positive and negative ions, and it increases with the increasing charge. Alonso and Cordero[40,41] observed that the function of the correlation energy and that of the number of antiparallel-spin electron pairs behave similarly with respect to the atomic number, and they suggested that the correlation energy should be proportional to the number of the opposite-spin electron pairs, $N_{\downarrow\uparrow}$. In their formulation, based on density functional theory (DTF) context, they focus on the decomposition of the correlation energy into the pairing energies and on their additivity. The correlation energy can be written using DFT formalism as:[16]

$$E_{corr}[\rho_{\uparrow}, \rho_{\downarrow}] \cong \frac{1}{2} \sum_{\sigma \neq \sigma'} \iint \rho_{\sigma}(\boldsymbol{r}_1) \frac{g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{\boldsymbol{r}_{12}} \rho_{\sigma'}(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \qquad (2.18)$$

where $\boldsymbol{r}_{12}$ is the inter-electronic distance, $g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the pair-correlation function for Coulomb correlation, and the quantity $\rho_{\sigma'}(\boldsymbol{r}_2) g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is interpreted as a Coulomb hole around an electron with spin σ at $\boldsymbol{r}_1$. For $\sigma \neq \sigma'$, the important contribution to the Coulomb hole comes from the correlation between the electrons with the opposite spins. The Coulomb hole between the parallel-spin electrons is very small in atomic systems as the Fermi correlation prevents the same spin electrons from occupying the same region in space. The pair correlation function is negative for small $\boldsymbol{r}_{12}$ and positive for large $\boldsymbol{r}_{12}$ which increases the probability of finding two antiparallel electrons at larger $\boldsymbol{r}_{12}$, and decreases the probability at small inter-electronic distance.[41]

The correlation energy of neutral and slightly charged positive and negative ions is linked to the number of the antiparallel spin electron pairs in the same main shell (K, L, …), while the inter-shell correlation energies are assumed minor, and their effect is approximately included within a single optimized parameter, that averages the pairing energy.[40]

$$E_{corr} = \alpha N_{\uparrow\downarrow} \tag{2.19}$$

The study includes atomic systems with $Z \leq 18$, but it is predicted that the linearity could be approximately valid for larger Z as well, although the correlation energy for heavier atoms might show the proportionality to $Z^{4/3}$ instead. The relationship between the atomic correlation energies and the number of the opposite-spin electron pairs has been extended to include the orbital dependency of pairing energies in the later work of Alonso *et. al*.[41] They found that the strength of the correlation depends on the overlap between the single-particle orbitals occupied by two electrons,[41] where a good spatial separation exists between the different main shells electrons (1s in *K* shell and 2s in *L* shell), while the same main shell orbitals overlap quite strongly in the same region of space (2s and 2p in *K* shell, for example). The overlap can be visualized using plots of the radial densities $r^2R^2(r)$, obtained from a DFT calculations with LDA, where $R(r)$ is the radial part of the wavefunction.[42] Consequently, the majority of the correlation energy between the parallel spin electrons would arise from the correlation between the electrons in the same main shell. These contributions can be separated into *ss*, *sp*, and *pp* correlations (within the first two shells), restricted to the electrons in the same main shell, and the magnitude of the pairing energies was found to follow $-E_{ss} > -E_{sp} > -E_{pp}$

ordering. Alonso *et. al.*[41] explained the above ordering in terms of two effects: the first effect involves the degree of the overlap between two orbitals involved; for example, the three *p* orbitals are oriented mutually perpendicular in space, so the wavefunction overlap between antiparallel spin electrons in different *p* orbitals is much smaller than the overlap between the *s* and any of the *p* orbitals of the same shell; therefore, the *sp* correlation is more important. The second involves radial localization of the orbitals, where for example 2*p* orbitals are less localized compared to 2*s* orbitals, and therefore the motion of the two antiparallel-spin 2*p* electrons would already be correlated more than that of the two 2*s* electrons.

While Alonso *et. al.*[41] showed that the correlation energy of low *Z* neutral atoms can be accurately modelled using the orbital-dependent pairing energies, they also explored a similar approach to the correlation energies of charged atomic systems. The behaviour is similar for singly charged cations and anions, except that the values of the slopes of the linear fit are not the same. The main difference is observed for the E_{ss} pairing energy, where the increase is seen for the cations (increased localization as a result of a decreased screening of the nuclear charge), while the decrease in E_{ss} pairing energy results for the anions (less localized due to extra screening of the nuclear charge).[41] The variation in E_{sp} pairing energy follows the opposite trend, and it is attributed to the *s*-wavefunction localization: increased *s* localization lowers the E_{sp} pairing energy while lowering the 2*s* and 2*p* orbital overlap.

McCarthy and Thakkar[43] proposed a couple of models for the correlation energy of neutral atoms and singly charged cations:

$$E_{corr} = a\frac{N_{\uparrow\downarrow}^{intra}}{N_{\uparrow\downarrow}}N^{\frac{3}{2}} + b\left(1 - \frac{N_{\uparrow\downarrow}^{intra}}{N_{\uparrow\downarrow}}\right)\frac{1}{\langle r\rangle_{HF}} \tag{2.20}$$

$$E_{corr} = a\frac{N_{\uparrow\downarrow}^{intra}}{N_{\uparrow\downarrow}}N^{\frac{3}{2}} + b\left(1 - \frac{N_{\uparrow\downarrow}^{intra}}{N_{\uparrow\downarrow}}\right)\frac{1}{\langle r\rangle_{HF}} + c\frac{N_{\uparrow\uparrow}}{N_{\uparrow\downarrow}}\frac{1}{\langle r\rangle_{HF}} \tag{2.21}$$

The $N_{\uparrow\downarrow}^{intra}/N_{\uparrow\downarrow}$ is the ratio of the number of intra-shell antiparallel spin electron pairs to the number of the total antiparallel spin electron pairs, and the $1/\langle r\rangle_{HF}$ is a moment of the HF electron density ρ with the normalization $\int \rho(\boldsymbol{r})d\boldsymbol{r} = N$, which contains the model's dependence on atomic number Z.[43] The second model includes the contribution to the total correlation energy from the parallel spin electron pairs through the ratio $N_{\uparrow\uparrow}/N_{\uparrow\downarrow}$, in which $N_{\uparrow\uparrow}$ is the total number of same spin electron pairs.

Following the work of Alonso *et.al.*[40] on the modelling of the atomic correlation energies using number of electrons (or number of antiparallel-spin electron pairs), and the work of Liu and Parr[44] based on the electron density at the nucleus, Mohajeri *et.al.*[45] explored the extension of a simple atomic model to the molecular systems. Using the coalescence nuclear-electron cusp condition on $\rho(r)$, they showed that the atomic correlation energy can be represented as:

$$E_{corr} = \lambda N^{\alpha} Z^{\beta} \tag{2.22}$$

$$ln\frac{E_{corr}}{N} = ln\,\lambda + \beta\, ln\, Z \tag{2.23}$$

and when using different powers of atomic number for different isoelectronic series they could obtain very accurate fits. Using an additivity scheme to derive the model for molecular correlation energies in terms of constituent atoms and number of electrons, they suggested following model:[45]

$$E_{corr(molecule)} = a\sum_{i} E_{corr(i)} + bN + c \qquad (2.24)$$

where the sum is extended over the exact correlation energies of all atoms in the molecule. They confirm that the correlation energy in molecules is larger than the sum of the correlation energies of its corresponding constituent atoms, and even though their molecular model is not of chemical accuracy, it is nevertheless useful and economical procedure to estimate correlation energies of closed-shell polyatomic systems.

2.2.4. Relating Density at the Nucleus to the Total Correlation Energy

Koga *et. al.*[46] pointed out that the electron density at the nucleus is almost the same for each cation, neutral atom, and anion for the same atomic number *Z*. The electron density at the nucleus can be modelled as almost entirely due to the *s*-type atomic orbitals, predominantly the 1*s* orbital. They showed that for the neutral atoms, and singly charged anions and cations, the hydrogenic approximation of each 1*s* electron contributing Z^3/π to the electron density at the nucleus reproduces HF values within 11% accuracy.[46] Following these results the idea that the correlation energy is related to the electrostatic potential at the nucleus was extended by Liu and Parr.[44] They report a simple empirical formula relating the electron density at the nucleus, $\rho(0)$ and the total electron correlation energy for simple atomic systems.

$$E_{corr} = CN\rho(0)/Z^{\gamma} \qquad (2.25)$$

where *Z* is the atomic number, *N* is the number of electrons, and γ and *C* are constants optimized for each isoelectronic atomic series, where both γ and *C* are irregular functions of *N*. The reasonably accurate (R^2 = 0.9435) fit has been reported for a large

data set of atomic series.[44] The accuracy of a simple relationship obtained in Liu and Parr's work is remarkable, as it is quite encouraging, especially if there could be a way to extend these simple models to the calculations on larger chemical systems, it is fairly reasonable to expect that different optimized coefficients would be determined for different isoelectronic atomic series. It would be interesting to investigate further relationship between the coefficients for each isoelectronic series with respect to *N*, and to determine the possible nature of the changes that occur with adding or removing an electron in each case.

According to the virial theorem, in quantum mechanics the average kinetic energy of an atom equals -½ times the average total potential energy:[47]

$$\langle T \rangle = -\frac{1}{2}\langle V_{total} \rangle \tag{2.26}$$

In accordance with the validity of the virial theorem for the total exact energy of a system, E_{exact}, and for the Hartree-Fock energy, E_{HF}, and using the classical definition of the correlation energy in eq. (2.1), Liu and Parr modelled the kinetic and the potential contributions to the correlation energy, T_{corr} and V_{corr}, separately.[44]

$$E_{corr} = -T_{corr} = \frac{1}{2}V_{corr} = T_{corr} + V_{corr} \tag{2.27}$$

$$T_{corr}(N,Z) = C_T N\rho(0)Z^{-1} = -E_{corr} \tag{2.28}$$

$$\frac{1}{2}V_{corr}(N,Z) = C_V N\rho(0)Z^{-2} = -E_{corr} \tag{2.29}$$

where the empirical values of C_T and C_V were determined for each isoelectronic series.

2.2.5. An *ab initio* Linear Electron Correlation Operator

The traditional density functional approach introduces nonlinear semi-empirical density dependent functionals to account for the electron correlation. Rassolov[48] proposed a linear correlation operator which modifies the Hartree-Fock Hamiltonian and which gives correlation energy for the single determinantal wavefunction in the form:

$$\hat{C} = -\frac{C_0}{r_{12}^2 p_{12}^2} \tag{2.30}$$

where r_{12} is the average distance between the electrons, p_{12} is the relative momentum operator, and C_0 is a numerical constant. The general functional form of the above operator was obtained by using determination of the correlation energy of two opposite systems: the dense electron gas, where the electrons are spread over the whole space, and the two-electron ion of high nuclear charge, where the electrons are localized close to the nucleus.[48] The correlation energy approaches a constant value as $Z \rightarrow \infty$ for a highly localized two-electron ion, when $r_{12}^2 \rightarrow 0$. The operator $\hat{C}$ has larger expectation value for the electrons that move along with each other ($p_{12}^2 \rightarrow 0$) than for the electrons with high relative momentum, as electrons that move fast with respect to each other would spend less time in each other's vicinity.[48]

2.3. Computational Methods and Approach

The focus of this thesis is to investigate the behavior of the correlation energy for a number of simple atomic and molecular systems and to report empirical models developed by our group in the past few years that are able to accurately predict the electron correlation energy for these systems. The work summarized here focuses

primarily on atomic systems; although, the electron correlation models of several small molecular systems have been investigated as well. The aim of these models is to describe the electron correlation as a function of several different variables; specifically, the variables obtained using computationally efficient Hartree-Fock method. The basis sets used in the calculations involving the atomic systems are large enough and scaled to obtain sufficiently reliable results; and therefore, the difference between the Hartree-Fock energy and the exact non-relativistic energy is due almost entirely to the inability of Hartree-Fock theory to account for the correlation energy, and thus the basis set incompleteness error is assumed to be very small and negligible in these cases. However, the small basis set used in the calculations involving molecular systems would add a non-negligible error in the calculated Hartree-Fock energy; therefore, the models suggested here account not only for the correlation energy in the molecular systems studied, but also for the basis set incompleteness error.

The aim of the correlation models presented here is to aid in the development of new theoretical methods that can treat electron correlation more accurately and efficiently. At the same time, these simple models inevitably add to the better understanding of electron correlation in atoms and molecules. It is interesting to note that these very simple, few-parameter models have the accuracy comparable to some of the more complex and computationally more expensive theoretical methods. The complexity of highly accurate methods makes them extremely costly computationally; thus, their use is often impractical, or in some cases impossible, when applied to large chemical systems. Currently, the computational study of macromolecules is frequently

limited to empirical methods, mainly due to their efficiency. The simple electron correlation models may prove quite useful in the study of large molecular systems offering higher accuracy compared to the existing empirical methods.

2.3.1. Methods Used to Model Atomic Systems

All the calculations were performed with MUNgauss[49] and Gaussian09.[50] The atomic energies were calculated at the HF level of theory (RHF for closed shell and ROHF for open shell systems) using the aug-cc-pVTZ basis set as implemented in Gaussian03,[51] where the scale factors were optimized for each system. The scaling factors were found to converge to a linear function of *Z*; therefore, the scale factors were constrained to be a linear function of *Z*. The equations used to define the scale factors for the systems studied are given in Table 2.1. The correlation energies of atomic systems are taken from the summary given by Chakravorty *et. al.*[28,29] and are listed in Table 2.2.

2.3.2. Methods Used to Model Molecular Systems

All the calculations were performed with MUNgauss[49] and Gaussian09.[50] The molecular systems were optimized at the HF level using 6-31G(d,p) basis set as implemented in Gaussian03;[51] the molecular energy of the optimized systems was further calculated at MP4, QCISD, and CCSD levels of theory for comparison. The correlation energies of the molecular systems are taken from the work of Gill *et. al.*,[22] and are listed in Table 2.3. Figure 2.3 shows the relationship of the correlation energy for the group of the molecular systems studied with number of electrons.

Table 2.1: Equations defining the scale factors, $\zeta_i = a_i Z + b_i$, for the atomic systems.

ζ_i	a	B	a	b	a	b
	He – Ni^{26+}		Li – Ni^{25+}		Be – Ni^{24+}	
ζ_1	0.2297	0.0558	0.2320	0.0666	0.2338	0.0495
ζ_2	0.2542	-0.1482	0.2562	-0.1705	0.2519	-0.0251
ζ_3	0.4727	-0.6575	0.5134	-0.9557	0.5187	-1.0800
ζ_4	0.4004	-0.2153	0.4013	-0.2045	0.4012	-0.1245
ζ_5	1.7443	1.3604	1.1344	-1.7911	1.1331	-1.8774
	B – Ni^{23+}		C – Ni^{22+}		N – Ni^{21+}	
ζ_1	0.3815	-0.7878	0.3785	-0.7045	0.3821	-0.7429
ζ_2	0.3939	-0.9864	0.3915	-0.9356	0.3941	-0.9863
ζ_3	0.3362	-0.8969	0.3386	-0.8417	0.3346	-0.6400
ζ_4	0.3275	-0.7993	0.3305	-0.7813	0.3367	-0.8098
ζ_5	0.2496	-0.1073	0.2501	-0.1233	0.2516	-0.1740
ζ_6	0.2893	-0.4781	0.2882	-0.5111	0.2902	-0.5859
ζ_7	0.6120	-1.6696	0.6158	-1.6637	0.6120	-1.5328
ζ_8	0.4535	-0.7222	0.4492	-0.7369	0.4533	-0.8696
ζ_9	1.2376	-2.6495	1.2470	-2.7487	1.2355	-2.6313

ζ_i	a	B	a	b	a	b
	O – Ni^{20+}		F – Ni^{19+}		Ne – Ni^{18+}	
ζ_1	0.3779	-0.6358	0.3708	-0.4792	0.3670	-0.3504
ζ_2	0.3868	-0.8501	0.3782	-0.6853	0.3740	-0.5512
ζ_3	0.3400	-0.4648	0.3462	-0.4085	0.3554	-0.4001
ζ_4	0.3390	-0.7088	0.3354	-0.4736	0.3371	-0.3783
ζ_5	0.2523	-0.1946	0.2539	-0.2511	0.2587	-0.3712
ζ_6	0.2943	-0.7233	0.2936	-0.7686	0.2977	-0.8531
ζ_7	0.6156	-1.6101	0.6167	-1.6254	0.6280	-1.8915
ζ_8	0.4582	-1.0568	0.4571	-1.1224	0.4639	-1.2583
ζ_9	1.2452	-2.9132	1.2316	-2.7225	1.2370	-2.9133

Table 2.2: Correlation energies[a] (in Hartrees) for the isoelectronic atomic systems.

	N=2	N=3	N=4	N=5	N=6	N=7	N=8	N=9	N=10
He	-0.0420								
Li	-0.0435	-0.0453							
Be	-0.0443	-0.0474	-0.0943						
B	-0.0447	-0.0486	-0.1113	-0.1249					
C	-0.0451	-0.0495	-0.1264	-0.1388	-0.1564				
N	-0.0453	-0.0501	-0.1405	-0.1505	-0.1666	-0.1883			
O	-0.0455	-0.0505	-0.1540	-0.1608	-0.1747	-0.1942	-0.2579		
F	-0.0456	-0.0508	-0.1671	-0.1704	-0.1816	-0.1988	-0.2611	-0.3245	
Ne	-0.0457	-0.0511	-0.1799	-0.1793	-0.1877	-0.2025	-0.2645	-0.3253	-0.3905
Na	-0.0458	-0.0514	-0.1925	-0.1879	-0.1932	-0.2056	-0.2677	-0.3275	-0.3889
Mg	-0.0459	-0.0515	-0.2049	-0.1961	-0.1982	-0.2081	-0.2705	-0.3300	-0.3896
Al	-0.0459	-0.0517	-0.2173	-0.2042	-0.2030	-0.2103	-0.2730	-0.3325	-0.3911
Si	-0.0460	-0.0518	-0.2295	-0.2121	-0.2075	-0.2121	-0.2753	-0.3347	-0.3928

	N=2	N=3	N=4	N=5	N=6	N=7	N=8	N=9	N=10
P	-0.0460	-0.0520	-0.2417	-0.2198	-0.2118	-0.2138	-0.2772	-0.3368	-0.3946
S	-0.0461	-0.0521	-0.2538	-0.2275	-0.2160	-0.2152	-0.2790	-0.3387	-0.3962
Cl	-0.0461	-0.0522	-0.2659	-0.2350	-0.2201	-0.2164	-0.2805	-0.3403	-0.3978
Ar	-0.0461	-0.0522	-0.2779	-0.2425	-0.2240	-0.2176	-0.2819	-0.3418	-0.3992
K	-0.0462	-0.0523	-0.2899	-0.2500	-0.2279	-0.2186	-0.2831	-0.3432	-0.4005
Ca	-0.0462	-0.0524	-0.3019	-0.2573	-0.2316	-0.2195	-0.2842	-0.3444	-0.4017
Sc	-0.0462	-0.0524	-0.3138	-0.2647	-0.2353	-0.2203	-0.2852	-0.3455	-0.4028
Ti	-0.0462	-0.0525	-0.3258	-0.2720	-0.2390	-0.2210	-0.2862	-0.3466	-0.4038
V	-0.0462	-0.0525	-0.3377	-0.2792	-0.2426	-0.2217	-0.2870	-0.3475	-0.4048
Cr	-0.0463	-0.0526	-0.3496	-0.2865	-0.2462	-0.2224	-0.2878	-0.3484	-0.4056
Mn	-0.0463	-0.0526	-0.3615	-0.2937	-0.2497	-0.2229	-0.2885	-0.3492	-0.4064
Fe	-0.0463	-0.0527	-0.3733	-0.3009	-0.2532	-0.2235	-0.2892	-0.3499	-0.4072
Co	-0.0463	-0.0527	-0.3852	-0.3080	-0.2566	-0.2240	-0.2898	-0.3506	-0.4079
Ni	-0.0463	-0.0527	-0.3970	-0.3152	-0.2601	-0.2244	-0.2903	-0.3512	-0.4085

[a]Correlation energies for the atomic systems are from reference (29).

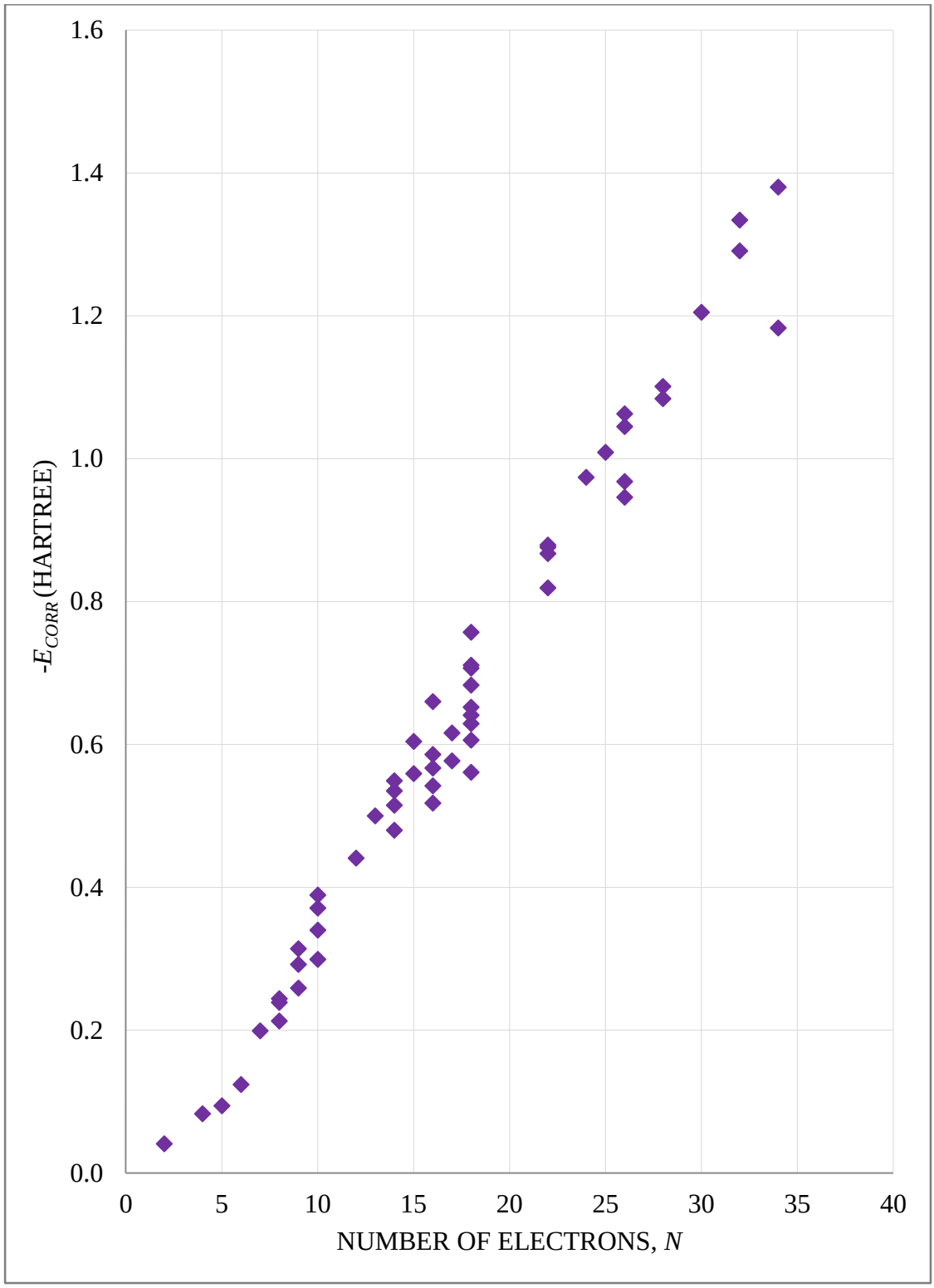


Figure 2.3. Correlation energies for the set of small molecular systems studied.

Table 2.3: Correlation energies[a] (in Hartrees) for the molecular systems studied.

	E_{corr}		E_{corr}		E_{corr}		E_{corr}
H_2	-0.041	FH	-0.389	H_2NNH_2	-0.641	SC	-0.867
LiH	-0.083	LiF	-0.441	HOOH	-0.711	SO	-0.974
BeH	-0.094	CN	-0.500	F_2	-0.757	ClO	-1.009
Li_2	-0.124	HCCH	-0.480	CO_2	-0.876	ClF	-1.063
CH	-0.199	HCN	-0.515	$SiH_2(^1A_1)$	-0.567	CH_3Cl	-0.968
$CH_2(^3B_1)$	-0.213	CO	-0.535	$SiH_2(^3B_1)$	-0.542	CH_3SH	-0.946
$CH_2(^1A_1)$	-0.239	N2	-0.549	SiH_3	-0.577	HOCl	-1.045
NH	-0.244	HCO	-0.559	PH_2	-0.616	Si_2	-1.084
CH_3	-0.259	NO	-0.604	SiH_4	-0.606	NaCl	-1.101
NH_2	-0.292	H_2CCH_2	-0.518	PH_3	-0.652	P_2	-1.205
OH	-0.314	H_2CO	-0.586	SH_2	-0.683	S_2	-1.291
CH_4	-0.299	O_2	-0.660	ClH	-0.707	SO_2	-1.334
NH_3	-0.340	H_3CCH_3	-0.561	Na_2	-0.819	Cl_2	-1.380
H_2O	-0.371	CH_3OH	-0.629	SiO	-0.879	Si_2H_6	-1.183

[a]Correlation energies for the molecular systems are from reference (22).

3. Simple Models for the Correlation Energy

3.1. Modelling of the Atomic Systems

3.1.1. The Expansion of the Electron Correlation in J^{-1}

Davidson and co-workers[28,29] estimated the expansion of the correlation energy for the isoelectronic series of 2 to 18 electrons using experimental and *ab initio* values. Each *N* dependent coefficient in the correlation expansion series is given by the difference between the *N* dependent coefficients in the expansion series of the exact non-relativistic energy (equation 2.6) and calculated HF energy (equation 2.5).

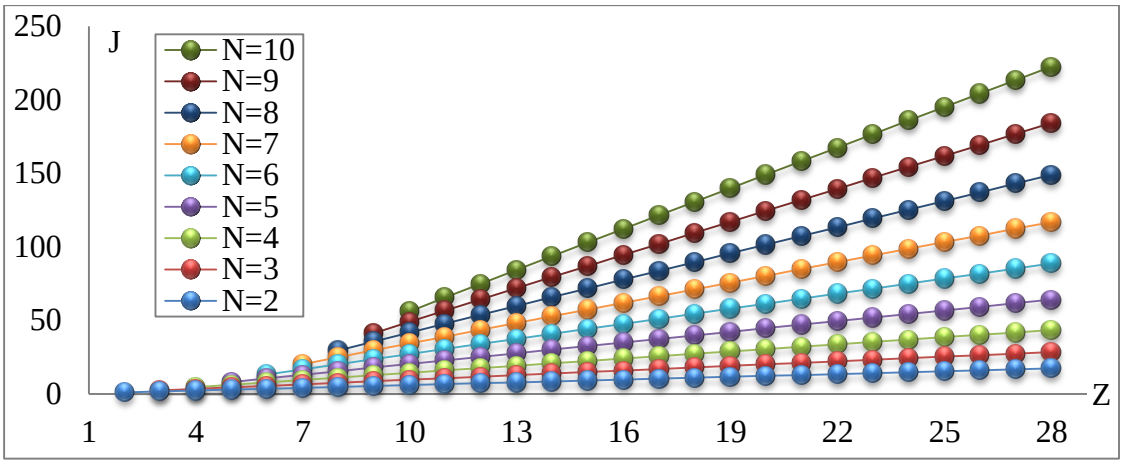
$$E_{corr}(N,Z) = \Delta B_1(N)Z^1 + \Delta B_2(N)Z^0 + \Delta B_3(N)Z^{-1} + \Delta B_4(N)Z^{-2} \qquad (3.1)$$

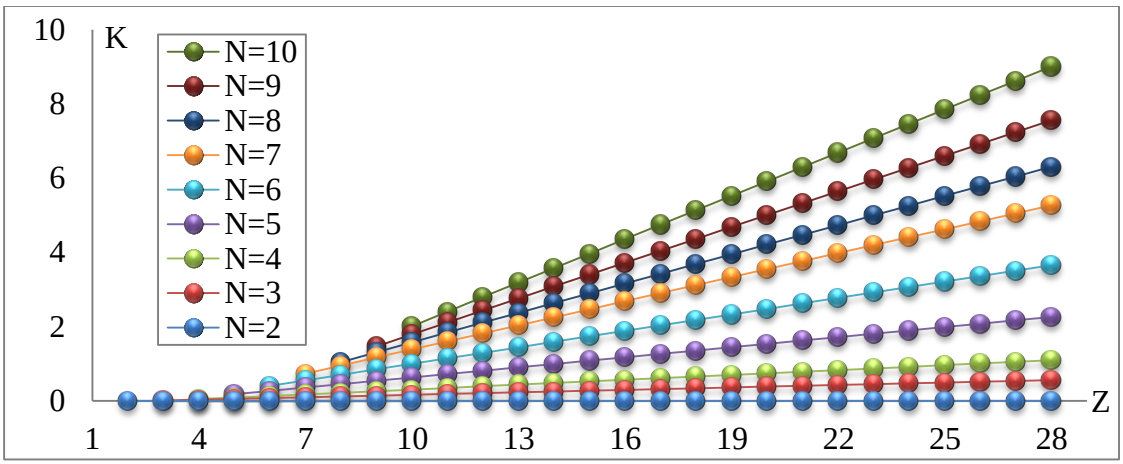
$$\Delta B_i(N) = B_i^{Exact}(N) - B_i^{HF}(N) \qquad (3.2)$$

The optimized coefficients for the truncated expansion are summarized in Table 3.1. For N=4, N=5, and N=6 isoelectronic systems the coefficient $\Delta B_1 \neq 0$, and the correlation energy expansion is linear in *Z*. Using the calculated HF results, it should be noted that the Coulomb energy ($J_{total} = J = \sum_{(i=1,j>i)}^{N} J_{ij}$), exchange energy ($K_{total} = K = \sum_{(i=1,j>i)}^{N} K_{ij}$), and also the square root of the kinetic energy ($\sqrt{T_{total}} = \sqrt{T} = \sum_{(i=1)}^{N} \sqrt{T_i}$) are all linear functions of *Z* (Figure 3.1). Using this relationship, it is possible to substitute Coulomb energy, J_{total} for *Z* in the correlation energy expansion:

Model A.I

$$E_{corr}(N,Z) = \Delta C_1(N)J^1 + \Delta C_2(N)J^0 + \Delta C_3(N)J^{-1} + \Delta C_4(N)J^{-2} \qquad (3.3)$$





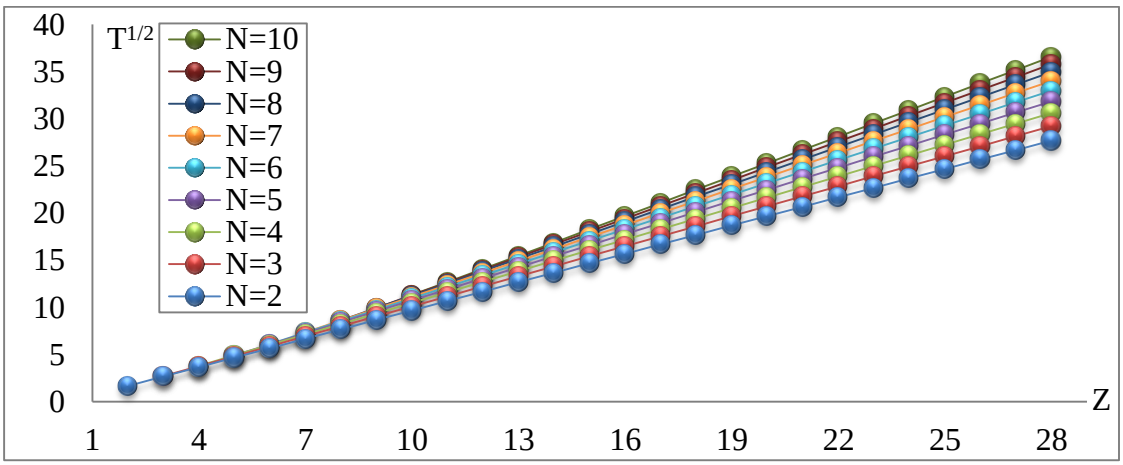


Figure 3.1. Coulomb energy (*J*), exchange energy (*K*), and the square root of the kinetic energy ($\sqrt{\boldsymbol{T}}$) (all given in a.u.) are all linear functions of *Z*.

Table 3.1: The coefficients ΔB_i (in a.u.) in the correlation energy expansion in Z^{-1}.

	ΔB_1	ΔB_2	$-\Delta B_3$	ΔB_4	RSS[a]
N=2	0.0000	0.0467	0.0101	0.0016	$0.7255E^{-10}$
N=3	0.0000	0.0537	0.0257	0.0018	$0.3884E^{-9}$
N=4	0.0117	0.0718	0.0886	-0.0354	$0.1891E^{-8}$
N=5	0.0070	0.1258	0.1423	-0.1820	$0.4067E^{-8}$
N=6	0.0031	0.1796	0.2078	-0.2680	$0.2168E^{-7}$
N=7	0.0000	0.2360	0.3410	0.0441	$0.8661E^{-9}$
N=8	-0.0003	0.3234	0.7618	2.0513	$0.2069E^{-6}$
N=9	-0.0007	0.4104	1.2913	5.1522	$0.7855E^{-6}$
N=10	-0.0012	0.4974	1.9442	9.8576	$0.1136E^{-5}$

[a]RSS is a residual sum of squares; RSS = TSS (total sum of squares) – ESS (explained sum of squares).

Table 3.2: The coefficients ΔC_i (in a.u.) in the correlation energy expansion in J^{-1}.

	ΔC_1	ΔC_2	$-\Delta C_3$	ΔC_4	RSS
N=2	0.0000	0.0466	0.0060	0.0013	$0.9445E^{-11}$
N=3	0.0000	0.0536	0.0252	0.0142	$0.3403E^{-9}$
N=4	0.0073	0.0844	0.1353	0.1326	$0.4375E^{-8}$
N=5	0.0029	0.1367	0.3536	0.5923	$0.1444E^{-8}$
N=6	0.0009	0.1855	0.7003	2.0648	$0.2452E^{-7}$
N=7	0.0000	0.2324	1.2649	7.3692	$0.3234E^{-7}$
N=8	0.0000	0.3049	2.4248	30.6213	$0.2166E^{-8}$
N=9	0.0000	0.3730	4.0177	84.1159	$0.4414E^{-7}$
N=10	0.0000	0.4355	5.8431	189.4843	$0.9499E^{-7}$

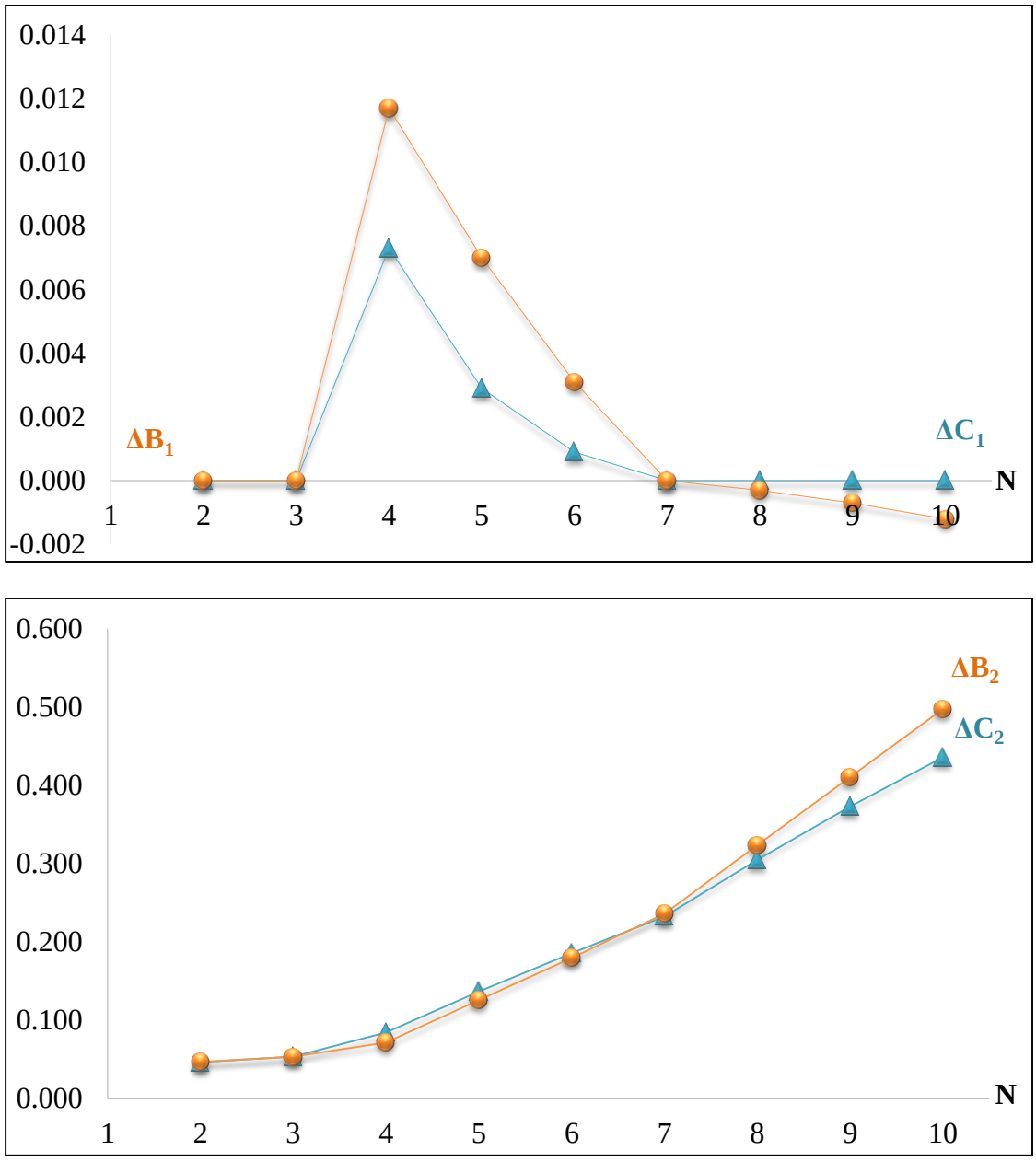


Figure 3.2a. The behavior of the optimized parameters (all given in a.u.) ΔB_i (yellow circles) and ΔC_i (blue triangles) (i = 1, 2) from the Taylor expansion of the correlation energy in $Z^{-1}$and in J^{-1}, respectively with respect to the number of electrons, N for the atomic systems for N=2 to N=10.

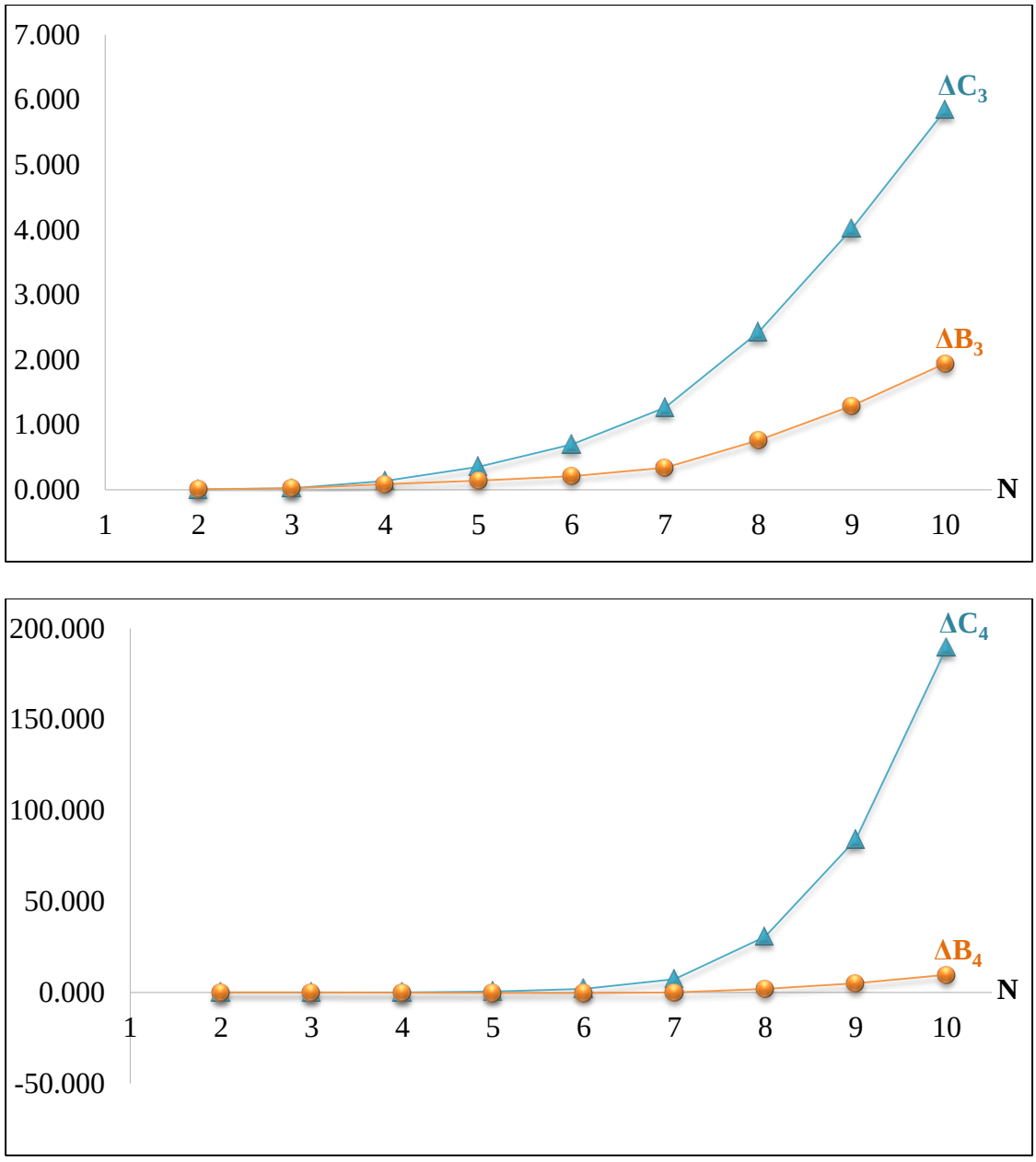


Figure 3.2b. The behavior of the optimized parameters (all given in a.u.) ΔB_i (yellow circles) and ΔC_i (blue triangles) (i = 3, 4) from the Taylor expansion of the correlation energy in $Z^{-1}$and in J^{-1}, respectively with respect to the number of electrons, N for the atomic systems for N=2 to N=10.

One advantage of the expansion of the correlation energy in J^{-1} over the expansion in Z^{-1} is that it would be applicable to the molecular systems as well as to the atomic systems in the modelling of correlation energy. The optimized coefficients for the truncated correlation energy expansion in J^{-1} are summarized in Table 3.2, and are compared to the coefficients in the correlation energy expansions in Z^{-1}. As expected, the coefficients ΔB_i and ΔC_i (i =1, 2, 3, 4) behave similarly with the changing number of electrons (Figures 3.2a and 3.2b). For the N=4, N=5, and N=6 isoelectronic systems, the coefficient $\Delta C_1 \neq 0$; therefore, the correlation energy is linear in Coulomb energy.

The linear dependence of J on Z could also be used to modify the correlation energy model described by Parr *et. al.*(equation 2.17) by the substitution of J for Z. For the H-atom and one-electron ions, the density at the nucleus, $\rho(0)$ is related to Z as:

$$\rho(0) \propto Z^3 \tag{3.4}$$

The above relationship can be approximately extended to other atomic systems (Figure 3.3), and the Liu-Parr model in equation 2.17 can be simplified to

$$E_{corr} = C^{Liu-Parr}(N) N Z^{(3-\gamma^{Liu-Parr})} \tag{3.5}$$

Using the linear dependence of J on Z, the correlation energy in atomic systems can be related to J, and expressed as:

Model A.II

$$E_{corr} = C^{Model\ A.II}(N)\, J^{\gamma^{Model\ A.II}} \tag{3.6}$$

The two parameters in the Liu-Parr model and the optimized parameters in Model A.II using Coulomb energy, are listed and compared in Table 3.3. Both parameters in Liu-Parr and in Model A.II depend on number of electrons present in the system, and

differ for each of the isoelectronic series. Figure 3.4 shows similar trends in the behavior of the $\gamma^{\text{Model A.II}}$ and $-\gamma^{\text{Liu-Parr}}$ parameters and the $C^{\text{Model A.II}}$ and $C^{\text{Liu-Parr}}$ parameters with respect to *N*. It is also evident that for the N=4 series the dependence of correlation energy on *J* and on *Z* is significantly different from that of the other series. These similar trends in the behavior of the coefficients in the expansion of correlation energy in Z^{-1}, in the Liu-Parr model, Model A.I and in Model A.II with the increasing number of electrons suggest that all of these models are inter-related by design through a dependence of the variables on the nuclear charge.

The relationship of the coefficients in the above models with the number of electrons, *N* is illustrated mainly to show the similar trends between the models. Although, the functions $\Delta B_i(N)$, $\Delta C_i(N)$, $C^i(N)$ and $\gamma^i(N)$ could be approximated and subsequently substituted into the equations presented, it is predicted that the extrapolation implemented this way could not lead to accurate results. The main reason for this is the periodicity observed in the correlation energy behaviour with *N*. Examining Figures 2.1 and Figure 2.2, one can deduce that the similarities exist between the $E_{correlation}$ functions for *N*=2, *N*=10 and *N*=18 (fully occupied shells), for *N*=3 and *N*=11 (one single electron in the *s* type orbital), for *N*=4 and *N*=12 (filled *s* type orbital, with empty *p* orbitals), for *N*=5, 6, 7 and *N*=13, 14, 15 (singly occupied *p* orbitals) and for *N*=8, 9, 10 and *N*=16, 17, 18 (doubly occupied *p* orbitals). Therefore, the correlation energy is not expected to be a smooth function of *N*, although, it likely is in certain *N* intervals, such as for *N*=5-7, *N*=7-10, or for *N*=13-15 and *N*=15-18, for example.

Table 3.3: The parameters in Liu-Parr model and in Model A.II (all given in a.u.)

	$C^{\text{Liu-Parr}}$	$\gamma^{\text{Liu-Parr}}$	$C^{\text{Model A.II}}$	$\gamma^{\text{Model A.II}}$	$RSS^{\text{Model A.II}}$
N=2	0.0467	3.0796	0.0432	0.0273	$3.003E^{-6}$
N=3	0.0302	3.0381	0.0451	0.0499	$7.070E^{-6}$
N=4	0.0166	2.3632	0.0289	0.6892	$6.208E^{-4}$
N=5	0.0209	2.5655	0.0439	0.4682	$3.933E^{-4}$
N=6	0.0292	2.7720	0.0776	0.2668	$5.203E^{-5}$
N=7	0.0446	2.9838	0.1450	0.0938	$5.209E^{-5}$
N=8	0.0518	2.9907	0.2009	0.0746	$1.296E^{-5}$
N=9	0.0591	3.0079	0.2600	0.0580	$8.713E^{-6}$
N=10	0.0664	3.0285	0.3291	0.0398	$2.737E^{-5}$

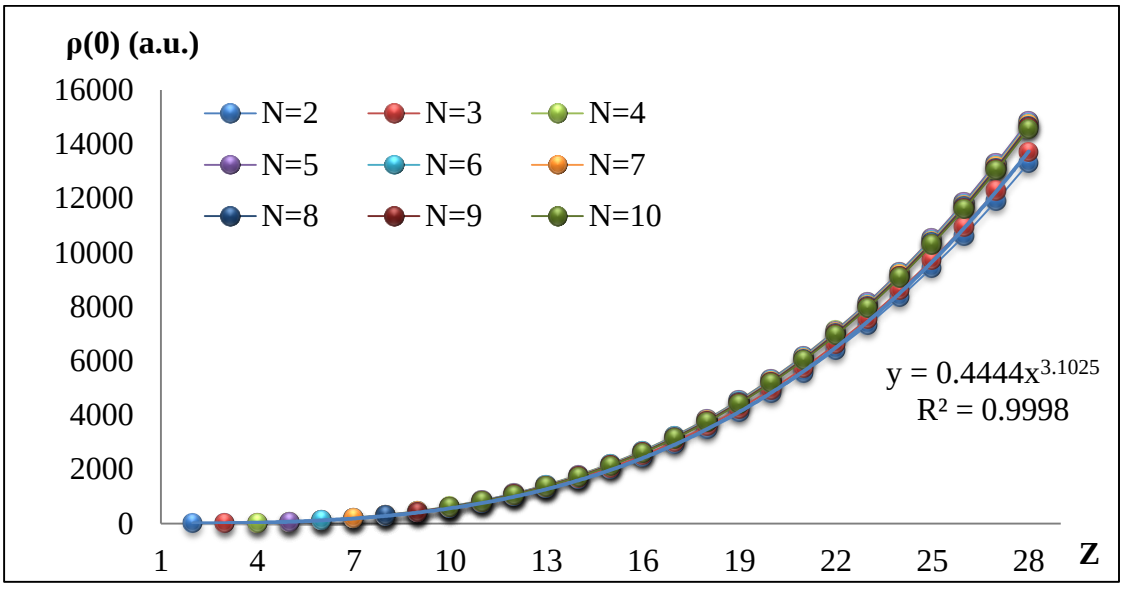


Figure 3.3. Density at the nucleus vs *Z* for isoelectronic atomic systems of *N*=2-10.

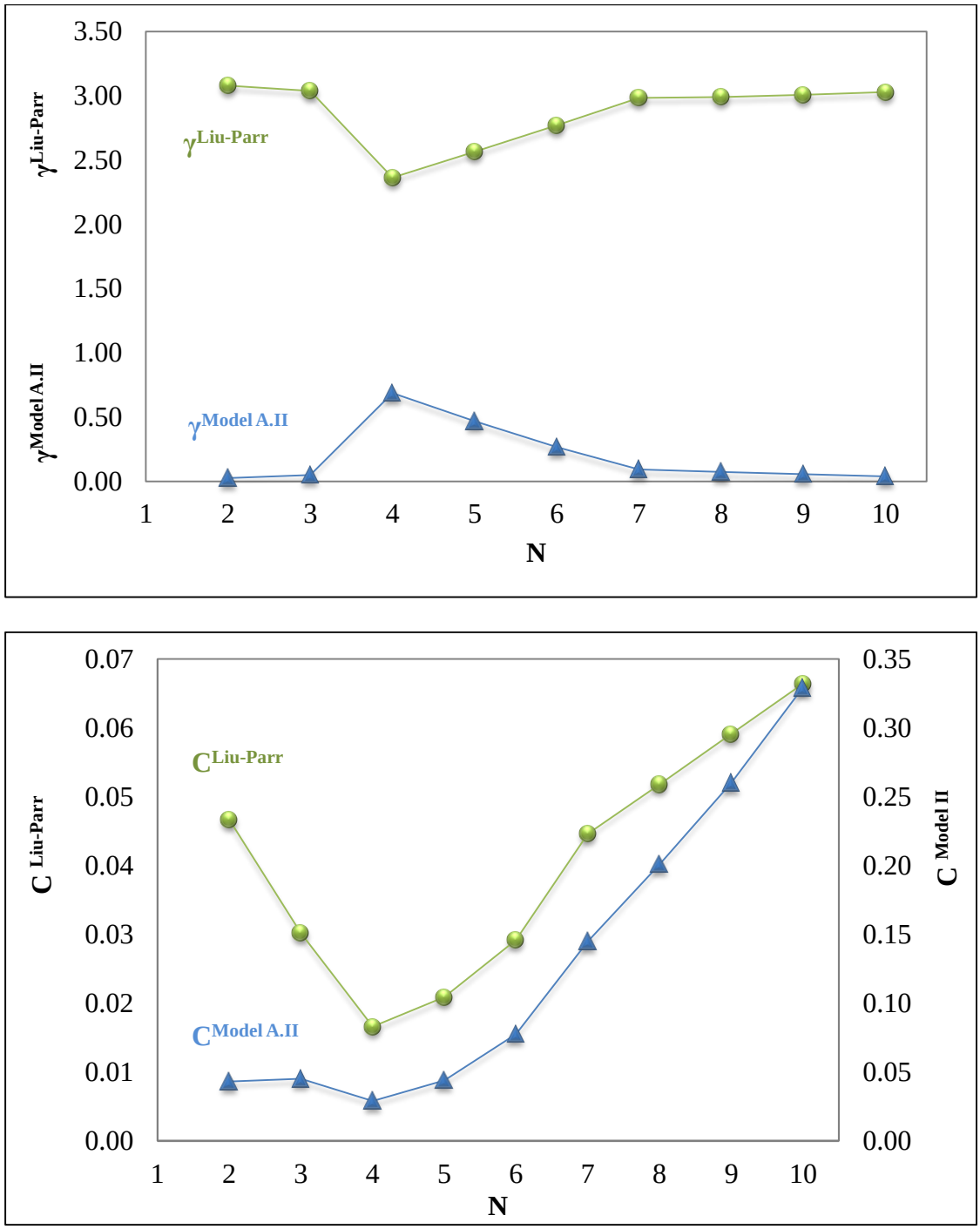


Figure 3.4. The parameters (in a.u.) $C^{Liu\text{-}Parr}$ and $\gamma^{Liu\text{-}Parr}$ in Liu-Parr model (green circles) and the parameters (in a.u.) $C^{Model\ A.II}$ and $\gamma^{Model\ A.II}$ in the Model A.II (blue triangles) vs number of electrons.

3.1.2. Correlation Energy as a function of Coulomb and Kinetic Energies.

Rassolov[52] proposed a linear correlation operator which gives the correlation energy for the single determinantal wavefunction based on its dependence on the two electrons' separation distance and their relative momentum (Equation 2.22). Starting with Rassolov's operator, it is possible to devise other simple electron correlation models based on the properties of HF orbitals and the total wavefunction for both atoms and molecules. In the following paragraph, the relationship between the correlation energy and the HF energies is explored for the atomic systems of N=2 to N=10 isoelectronic series. Replacing the expectation values of the separation distance r_{12}^2 and the relative momentum p_{12}^2 operators in the Rassolov's correlation operator by the average inter-particle distance and by the average inter-particle momentum, respectively, we arrive at:

$$(\delta r_{12})_{ab} = \sqrt{\langle ab|r_{12}^2|ab\rangle} \equiv \delta r_{ab} \tag{3.7}$$

$$(\delta p_{12})_{ab} = \sqrt{\langle ab|p_{12}^2|ab\rangle} \equiv \delta p_{ab} \tag{3.8}$$

$$E_{corr}^{ab} = \frac{C_0^{ab}}{(\delta r_{12})_{ab}(\delta p_{12})_{ab}} \tag{3.9}$$

Poirier and Hollett[34] observed that the average distance between two electrons, with one occupying molecular orbital a and another occupying molecular orbital b, $(\delta r_{12})_{ab}$ is inversely proportional to the two-electron Coulomb integral

$$J_{ab} = \frac{\alpha}{(\delta r_{12})_{ab}} \tag{3.10}$$

Using the above relationship for the average inter-particle distance and using the kinetic energy expression for the average inter-particle momentum:

$$\frac{1}{(\delta r_{12})_{ab}} = \frac{\alpha}{J_{ab}} \tag{3.11}$$

$$(\delta p_{12})_{ab} = \sqrt{2m_e}\sqrt{T_{aa} + T_{bb}} \tag{3.12}$$

With m_e=*1a.u.* the correlation energy for a given electron pair associated with molecular orbitals *a* and *b* becomes:

$$E_{corr}^{ab} = C^{ab}\ \frac{J_{ab}}{\sqrt{T_{aa} + T_{bb}}} \tag{3.13}$$

*T*he total correlation energy can be written as a sum of the pair correlation energies:

$$E_{corr} = \sum_{ab} C^{ab}\ \frac{J_{ab}}{\sqrt{T_{aa} + T_{bb}}} \tag{3.14}$$

where C^{ab} would differ from the value of C_0 in the Rassolov operator, and the parameter C^{ab} depends on the number of electrons of the system. For simplicity, a new variable X_{ab} was defined as

$$X_{ab} = \frac{J_{ab}}{\sqrt{T_{aa} + T_{bb}}} \tag{3.15}$$

and the relationship between the correlation energy and the variable X_{ab} was examined: For two electron series $\sum X_{ab} = X_{11}$, and therefore

$$E_{corr} \propto X_{11}\ , \qquad X_{11} = \frac{J_{11}}{\sqrt{2T_{11}}} \tag{3.16}$$

For two electron systems the behavior the of the parameter X_{11} with the increasing nuclear charge resembles that of the behavior of the correlation energy with the increasing *Z* (Figure 3.5) and the correlation energy for two electron series was fitted as

a linear function of X_{11}. Interestingly, the parameter X_{11} for the other isoelectronic series follows a similar trend with respect to correlation energy behavior with the increasing nuclear charge, except for the atomic series containing four, five, and six electrons. Figure 3.6 shows the relationships of each of the X_{11} vs Z and compares it to the E_{corr} vs Z behavior for all of the isoelectronic series. It was therefore initially investigated whether the total correlation energy for the atomic systems could be approximated using the X_{11} relationship:

Model A.III

$$E_{corr} = a(N)\, X_{11} + b(N) \tag{3.17}$$

The unique behavior of the correlation energy for the N=4, N=5, and N=6 electron series could be modelled more accurately using the modified Model A.III$_a$, where we included a linear function of J_{11}.

Model A.III$_a$

$$E_{corr} = a(N)\, X_{11} + b(N) + \; c(N)\, J_{11} \tag{3.18}$$

The resulting fits and the optimized parameters are summarized in Table 3.4. Successfully expressing total correlation energy of an atomic system using the ratio of the HF values for the core electrons only; specifically, the parameters J_{11} and T_{11}, suggests a possibility that the major part of the correlation energy of an atomic systems can be accounted from the correlation between the core electrons. It closely resembles an idea of Liu and Parr[44] who related the total correlation energy to the density at the nucleus, and assumed that the total correlation of an atomic system can be expressed using the properties of the electrons closest to the nucleus.

However, it is reasonable to expect that the accuracy of the above model could be improved by considering the correlation between other electron pairs in the system in addition to the correlation of the core electrons. Total Coulomb energy was used as a parameter where the correlation energies of the isoelectronic series were fitted to:

Model A.III$_b$

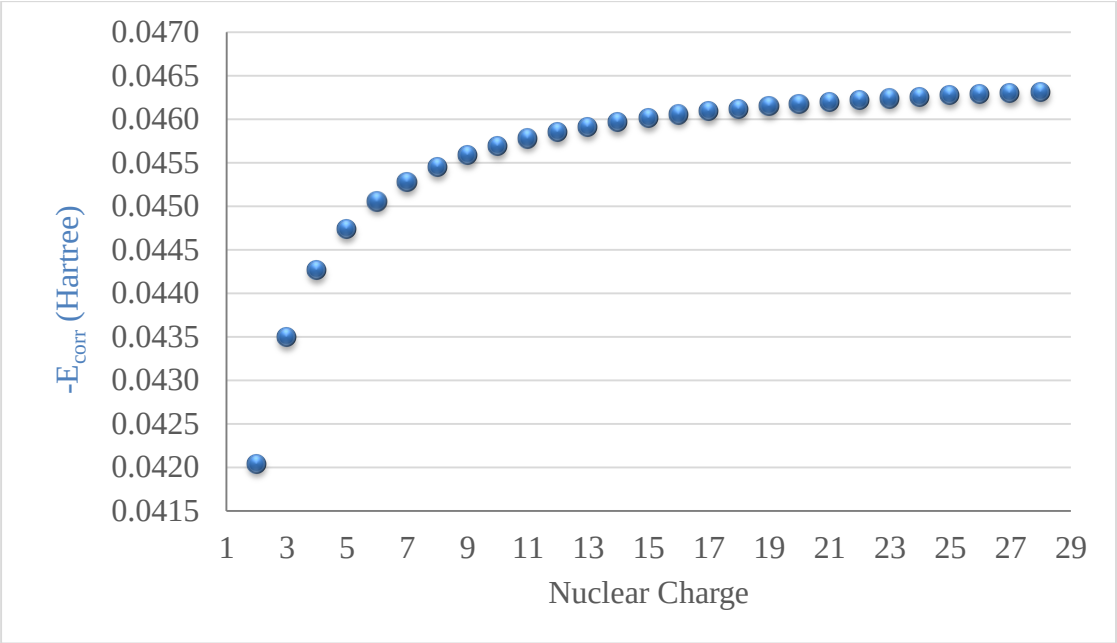
$$E_{corr} = a(N)\sum_{ab} J_{ab} + b(N) + c(N)/\sum_{ab} J_{ab} \tag{3.19}$$

The results are summarized in Table 3.5, while the behavior of the optimized coefficients with *N* is illustrated in Figure 3.7. These trends resemble the trends observed earlier with regards to the coefficients ΔB_i and ΔC_i in the expansion of the correlation energy in $1/Z$ and $1/J$, respectively. Specifically, $c(N)$ behaves like $\Delta B_1(N)$ and $\Delta C_1(N)$, while $-b(N)$ behaves like $\Delta B_2(N)$ and $\Delta C_2(N)$ with increasing *N*; arising from the dependence of the Coulomb energy on nuclear charge.

After several trials and fittings, a smaller number of models was considered, and these are described in the following paragraph. Initially, the contribution from each electron pair was weighted equally; and the total correlation energies for the isoelectronic series with *N*=2 to *N*=10 were fitted as a linear functions of a sum of the variables X_{ab}, where the sum includes the contribution from all of the electron pairs in the system, including the parallel-spin electron pairs.

Model A.IV.

$$E_{corr} = C(N)\sum_{ab} X_{ab} + c(N) \tag{3.20}$$



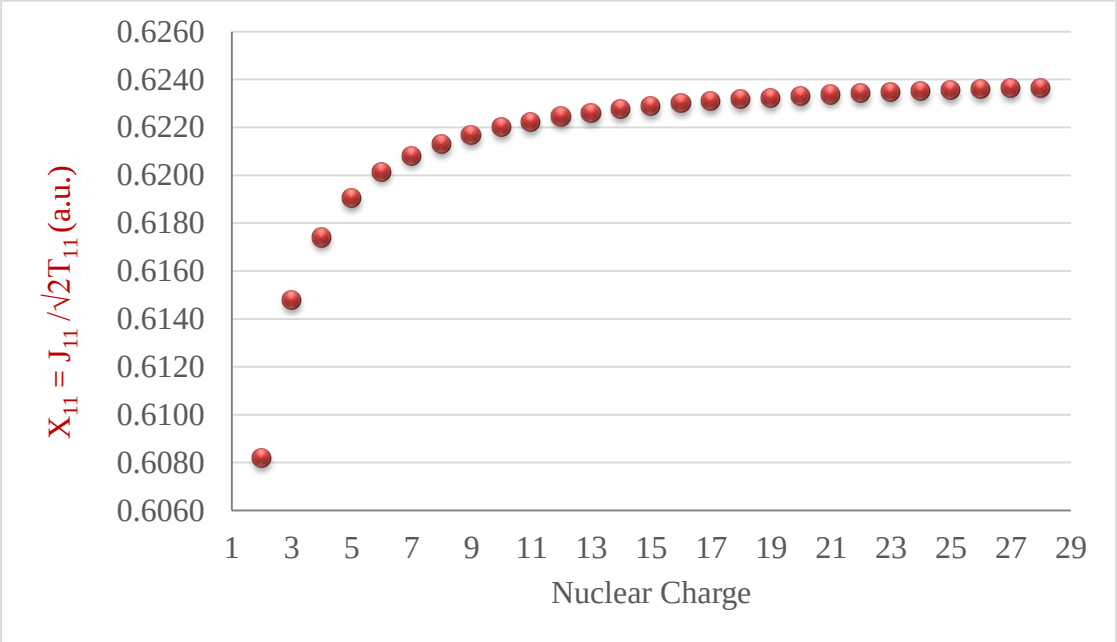


Figure 3.5. X_{11} vs Z relationship compared to the E_{corr} vs Z behavior for the atomic systems with N=2.

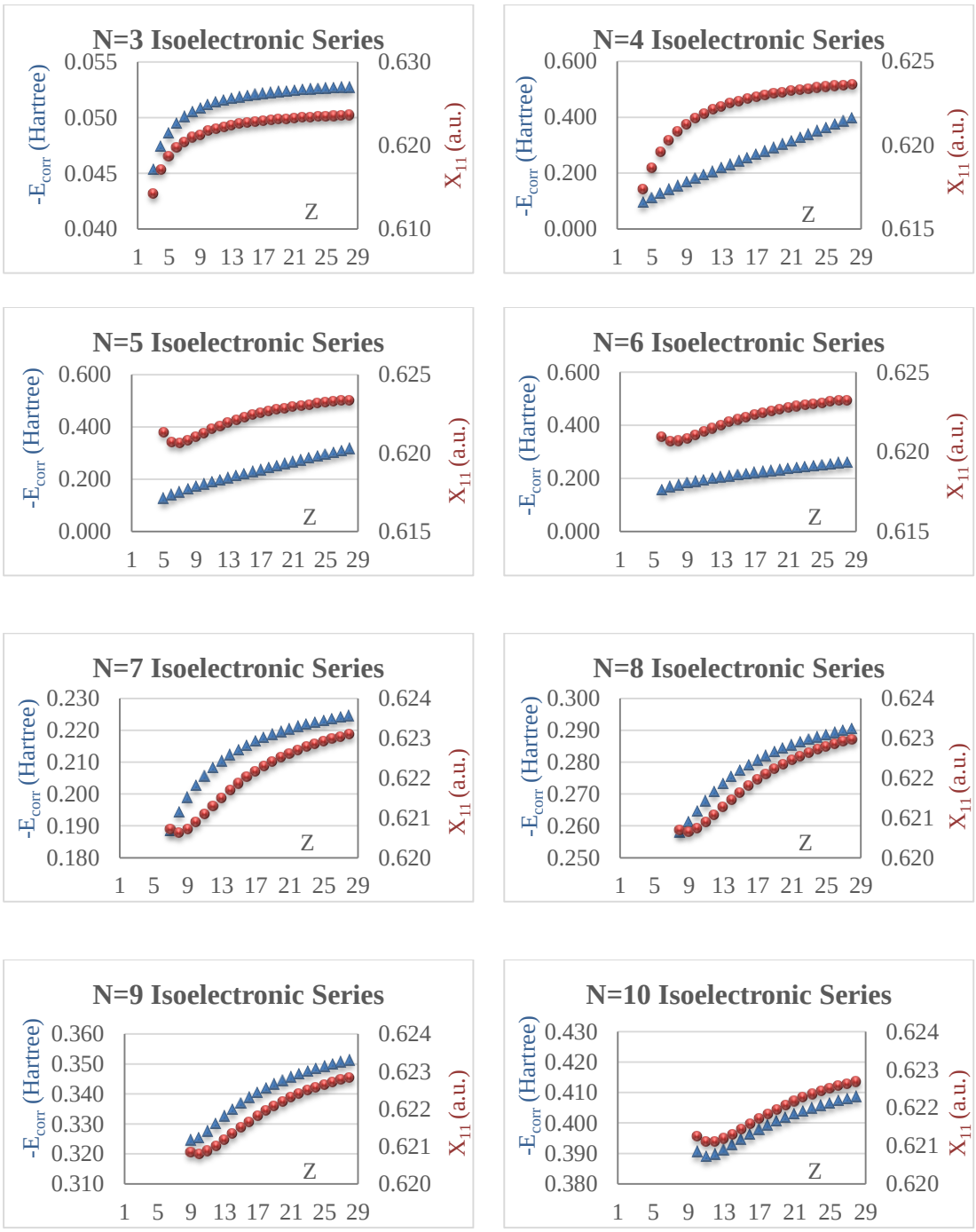


Figure 3.6. E_{corr} vs Z behavior (blue triangles, primary axes) compared to the $X_{11} = J_{11}/\sqrt{2}T_{11}$ vs Z relationship (red circles, secondary axes) for N=3-10 isoelectronic series.

Table 3.4: The optimized coefficients in Model A.III and Model A.III$_a$. (in a.u.)

	Model A.III			Model A.III$_a$			
	a(N)	*b(N)*	RSS	*a(N)*	*b(N)*	*c(N)*	RSS
N=2	0.2894	-0.1342	2.67E^{-7}	0.2632	-0.1182	0.0000	8.55E^{-8}
N=3	0.8040	-0.4487	1.03E^{-7}	0.7784	-0.4329	0.0000	6.20E^{-8}
N=4	49.4232	-30.496	3.81E^{-2}	3.6076	-2.1747	0.0186	8.79E^{-7}
N=5	59.3356	-36.693	4.99E^{-3}	2.1072	-1.2069	0.0123	3.40E^{-4}
N=6	33.2002	-20.438	7.34E^{-4}	8.7398	-5.2749	0.0052	3.10E^{-4}
N=7	11.6794	-7.0513	1.65E^{4}	15.1406	-9.1965	-0.0007	1.58E^{-5}
N=8	12.1092	-7.2522	6.85E^{-5}	15.5192	-9.3651	-0.0007	6.45E^{-5}
N=9	12.2680	-7.2890	2.16E^{-5}	14.6182	-8.7455	-0.0005	2.05E^{-5}
N=10	11.9688	-7.0440	5.51E^{-6}	9.9844	-5.8136	0.0003	4.98E^{-6}

Table 3.5: The optimized coefficients in Model A.III$_b$. (in a.u.)

	a(N)	*b(N)*	*c(N)*	RSS
N=2	-0.0045	-0.0463	0.0000	$5.49E^{-8}$
N=3	-0.0175	-0.0526	0.0000	$2.18E^{-7}$
N=4	-0.0974	-0.0818	0.0073	$9.35E^{-7}$
N=5	-0.2530	-0.1323	0.0029	$1.58E^{-6}$
N=6	-0.4769	-0.1790	0.0010	$2.07E^{-6}$
N=7	-0.7235	-0.2213	0.0000	$3.57E^{-6}$
N=8	-0.8144	-0.2806	0.0001	$1.03E^{-5}$
N=9	-0.7288	-0.3353	0.0001	$1.52E^{-5}$
N=10	-0.1627	-0.3846	0.0001	$1.67E^{-5}$

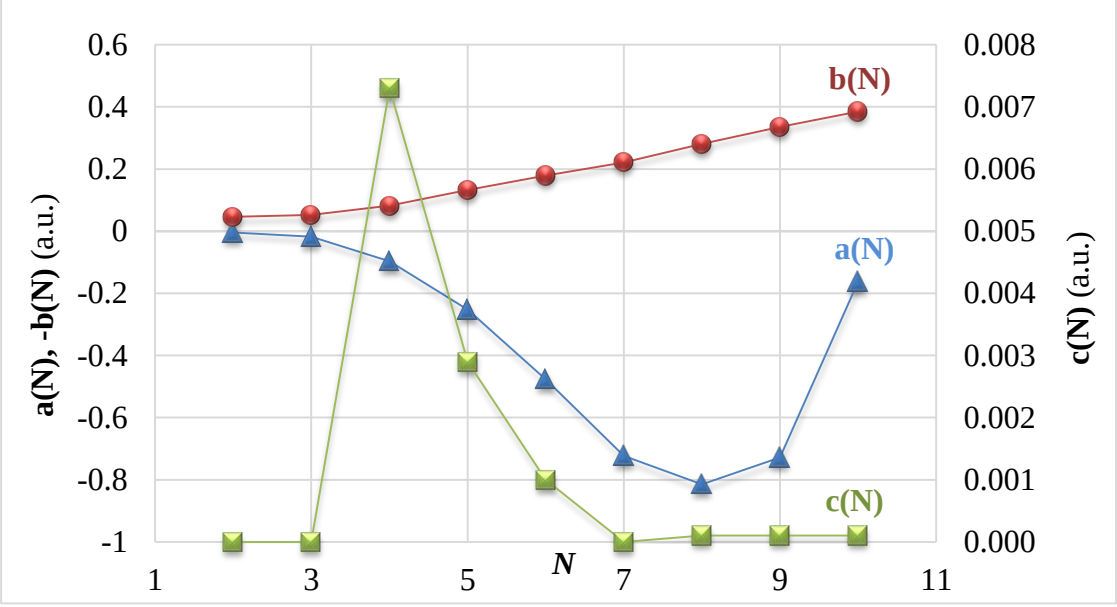


Figure 3.7. The relationship between the coefficients a(N) (blue triangles), b(N) (red circles) and c(N) (green squares) of Model A.III$_b$ vs *N*.

The accuracy of the fitting is reasonable, considering the simplicity of the model. As the parallel-spin electrons are already correlated in Hartree-Fock theory through the exchange correlation, it is assumed that the contribution of the parallel-spin electron pairs to the total Coulomb correlation energy could be neglected and the total correlation energy was fitted as a linear function of the sum of the variables Xab, where the sum includes the contribution from the opposite-spin electron pairs only. The total correlation energy was fitted as a linear function of the sum of the variables Xaa, where the sum includes the contribution from the opposite-spin electron pairs in the same shell only.

Model A.IV$_a$

$$E_{corr} = C'(N) \sum_{ab} X_{ab}^{1\downarrow} + c'(N) \tag{3.21}$$

The correlation energy for the atomic systems was fitted as:

Model A.IV$_b$

$$E_{corr} = C''(N) \sum_{a} X_{aa}^{1\downarrow} + c''(N) \tag{3.22}$$

The optimized parameters are summarized in Table 3.6 with the residual sum of squares values (RSS) in Table 3.7. The accuracies of Model A.IV, Model A.IV$_a$ and Model A.IV$_b$ are comparable to that of Model A.III. The behavior of the coefficients *C(N)* and *c(N)* with the increasing number of electrons follows similar trends for all of the models described above and all of them indicate different relationship for the *N*=4, *N*=5, and *N*=6 electron series. It is obvious that the above models are not sufficient to describe the correlation energy for the *N*=4, *N*=5, and *N*=6 electron series as accurately

as for the other *N* electron series. It appears that an additional term in the model function is needed to describe this behavior more accurately. At the same time; while the models A.III, A.IV, A.IV$_a$, and A.IV$_b$ treat each of the electron pairs likewise by using the same coefficient for all pairs, it is reasonable to assume that if the electron pair correlation was described separately for each different electron pair, the accuracy would increase. Using additional coefficients results in more complicated models as it increases the number of empirical parameters; however, it does improve a model.

Total atomic correlation energy can be partitioned into three parts: the correlation energy corresponding to the opposite spin electrons in the same orbital ($E^{1\downarrow}_{corr\_aa}$), the correlation energy corresponding to the opposite spin electrons in different orbitals ($E^{1\downarrow}_{corr\_ab}$), and the correlation energy corresponding to the parallel spin electrons ($E^{11}_{corr\_ab}$):

$$E_{corr} = \sum_{a} E^{1\downarrow}_{corr\_aa} + \sum_{ab} E^{1\downarrow}_{corr\_ab} + \sum_{ab} E^{11}_{corr\_ab} \qquad (3.23)$$

In the model described below, the E_{corr_aa} was modelled as a linear function of the sum of the X_{aa} parameters corresponding to pairs of the electrons in the same orbital (opposite spin). $E^{1\downarrow}_{corr\_ab}$ was related to a sum of the X_{ab} parameters corresponding to pairs of the electrons in different orbitals, while the $E^{11}_{corr\_ab}$ was modelled as a function of a modified X_{ab} parameter:

$$X^{11}_{ab} = (J_{ab} - K_{ab})/\sqrt{(T_{aa} + T_{bb})} \qquad (3.24)$$

Table 3.6: The optimized parameters for Models A.IV, A.IVa, and A.IVb. (in a.u.)

	C(N)	*c(N)*	*C′(N)*	*c′(N)*	*C″(N)*	*c″(N)*
N=2	0.2894	-0.1342	0.2894	-0.1342	0.2894	-0.1342
N=3	0.0404	0.0065	0.0769	-0.0153	0.8040	0.4487
N=4	1.1466	-1.9270	5.2161	-3.4428	-9.2900	8.9201
N=5	0.4386	-1.1246	1.8652	-1.6451	-7.3100	7.0471
N=6	0.1740	-0.5839	0.7420	-0.7460	-5.1882	5.0547
N=7	0.0480	-0.0953	0.2103	-0.1200	-2.3128	2.3700
N=8	0.0348	-0.0215	0.1403	-0.0579	2.4610	-2.9518
N=9	0.0242	0.0712	0.0932	0.0413	0.424	-0.7451
N=10	0.0146	0.1950	0.0555	0.1766	0.2716	-0.1613

Table 3.7: Residual Sum of Squares for Models A.IV, A.IV$_a$, and A.IV$_b$. (in a.u.)

	$RSS^{Model\ A.IV}$	$RSS^{Model\ A.IVa}$	$RSS^{Model\ A.IVb}$
N=2	$2.67E^{-7}$	$2.67E^{-7}$	$2.67E^{-7}$
N=3	$1.35E^{-6}$	$1.26E^{-6}$	$1.03E^{-7}$
N=4	$5.46E^{-2}$	$5.22E^{-2}$	$7.49E^{-2}$
N=5	$1.52E^{-2}$	$1.49E^{-2}$	$1.99E^{-2}$
N=6	$2.53E^{-3}$	$2.44E^{-3}$	$3.21E^{-3}$
N=7	$2.64E^{-5}$	$2.09E^{-5}$	$3.11E^{-5}$
N=8	$6.74E^{-5}$	$6.81E^{-5}$	$4.58E^{-5}$
N=9	$9.54E^{-5}$	$9.94E^{-5}$	$2.44E^{-4}$
N=10	$1.11E^{-4}$	$1.15E^{-4}$	$1.88E^{-4}$

Model A.V

$$E_{corr} = C_{aa}(N)\sum_{a} X_{aa}^{1\text{l}} + C_{ab}^{1\text{l}}(N)\sum_{ab} X_{ab}^{1\text{l}} + C_{ab}^{11}(N)\sum_{ab} X_{ab}^{11} \qquad (3.25)$$

The optimized parameters and the residual sum of squares (RSS) values for Model A.V are summarized in Table 3.8. There is not a considerable improvement over the simpler models with the increased number of the optimized coefficients; mostly, it still does not correctly account for the correlation energy of the *N=4*, *N=5*, and *N=6* series.

Alternatively, it could be argued that the *N* dependence should come through the number of the electron pairs accounted for in the summation. Model A.V was modified in such a way that the optimized coefficients were kept constant throughout the *N=2 – N=10* electron series, but in order to successfully fit the correlation energy for all of the isoelectronic series using the model function for each of the electron pair type, additional coefficient had to be included, Model A.V$_a$ (Table 3.9). This linear coefficient could possibly be related to the correlation energy limit for each of the *N* series with nuclear charge $Z\rightarrow\infty$. The correlation energy limiting values at $Z\rightarrow\infty$ limits were further explored in the relations to the limiting values of X_{ab} parameters at high *Z*. The attempts were made to relate the individual limits in X_{ab} parameters to the corresponding pair correlation energies, as well as considering the sum of these limits with respect to the total correlation energy limit for each of the series. These relationships could help to estimate a limiting value of the dynamical correlation energy for the isoelectronic systems containing four, five, and six electrons without the effects of the non-dynamical correlation present in these systems. Subsequently, finding a suitable model function for the Coulomb electron correlation energy in these systems might enable certain

separation of the dynamical and non-dynamical correlations in these systems, and consequently give an indication how to model the non-dynamical correlation more accurately, which was further explored in the subsequent section of this thesis. The relationships and the behavior of the correlation energy and the parameters X_{ab} with the increasing Z are illustrated in Figure 3.8, while the values of the limits at $Z \rightarrow \infty$ for each are summarized in Table 3.10, and their behavior with the increasing N are shown in Figure 3.9 and Figure 3.10. These results might turn out to be useful and aid in better understanding of the correlation energy behavior with the increasing number of electrons in the atomic systems as $Z \rightarrow \infty$.

Table 3.8: The optimized parameters for Model A.V. (in a.u.)

	$C_{aa\_\downarrow\uparrow}$	$C_{ab\_\downarrow\uparrow}$	$C_{ab\_\uparrow\uparrow}$	RSS
N=2	0.0734	-	-	$1.43E^{-5}$
N=3	0.0786	0.5325	-0.5760	$1.91E^{-8}$
N=4	2.8511	102.1663	-123.2810	$1.55E^{-2}$
N=5	0.8378	43.0581	-49.1328	$1.69E^{-3}$
N=6	1.6505	17.0164	-8.6586	$3.85E^{-4}$
N=7	0.2465	0.5233	-0.4055	$2.05E^{-7}$
N=8	0.4928	3.4385	-3.6171	$1.12E^{-5}$
N=9	0.1544	-3.9424	4.433	$1.18E^{-5}$
N=10	0.1793	-3.6580	4.0873	$6.52E^{-6}$

Table 3.9: The optimized parameters for Model A.V$_a$. (in a.u.)

	$C_{aa\_\downarrow\uparrow}$	$C_{ab\_\downarrow\uparrow}$	$C_{ab\_\uparrow\uparrow}$	c	RSS
N=2	0.0734	-	-	-	$1.43E^{-5}$
N=3	0.0734	0.5208	-0.4105	-0.0306	$1.59E^{-4}$
N=4	0.0734	0.5208	-0.4105	0.1476	$1.87E^{-1}$
N=5	0.0734	0.5208	-0.4105	-0.0089	$5.25E^{-2}$
N=6	0.0734	0.5208	-0.4105	0.4486	$3.46E^{-2}$
N=7	0.0734	0.5208	-0.4105	0.1814	$2.57E^{-7}$
N=8	0.0734	-3.2838	3.6831	-0.9512	$3.03E^{-3}$
N=9	0.0734	-3.2838	3.6831	0.1900	$2.46E^{-4}$
N=10	0.0734	-3.2838	3.6831	0.1479	$5.12E^{-6}$

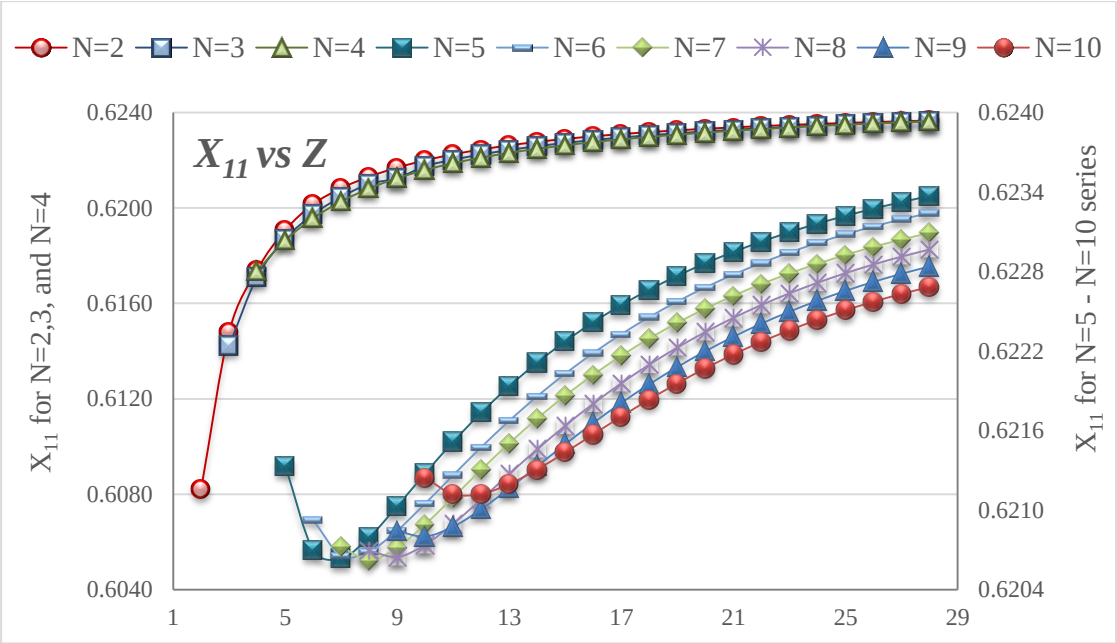


Figure 3.8a. Relationship X_{11} vs Z for the N=2 to N=10 isoelectronic series. (in a.u.)

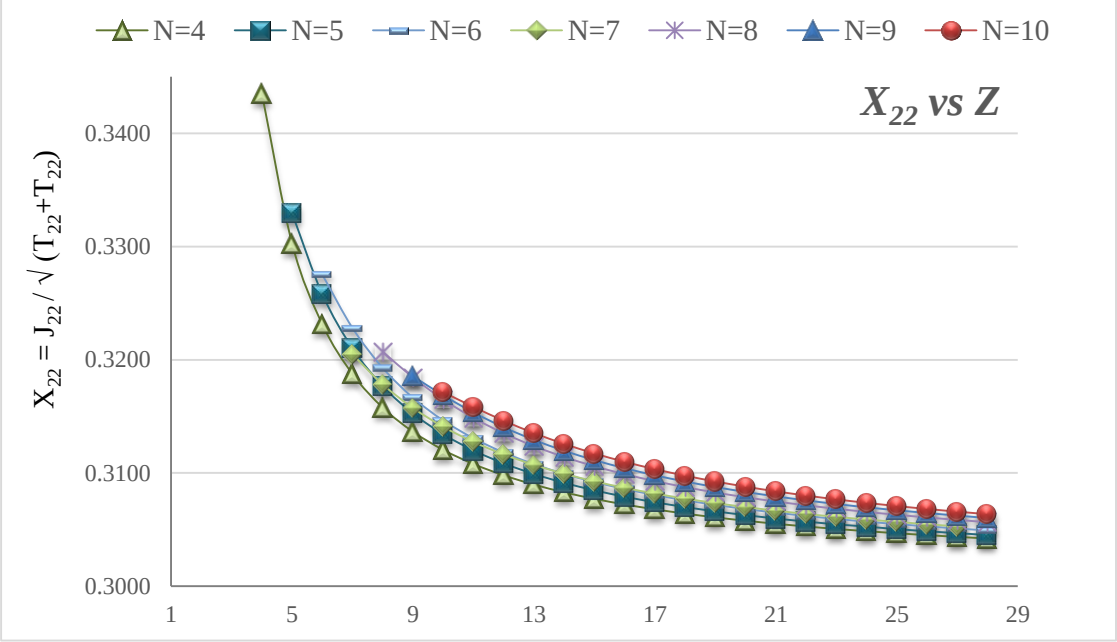


Figure 3.8b. Relationship X_{22} vs Z for the N=3 to N=10 isoelectronic series. (in a.u.)

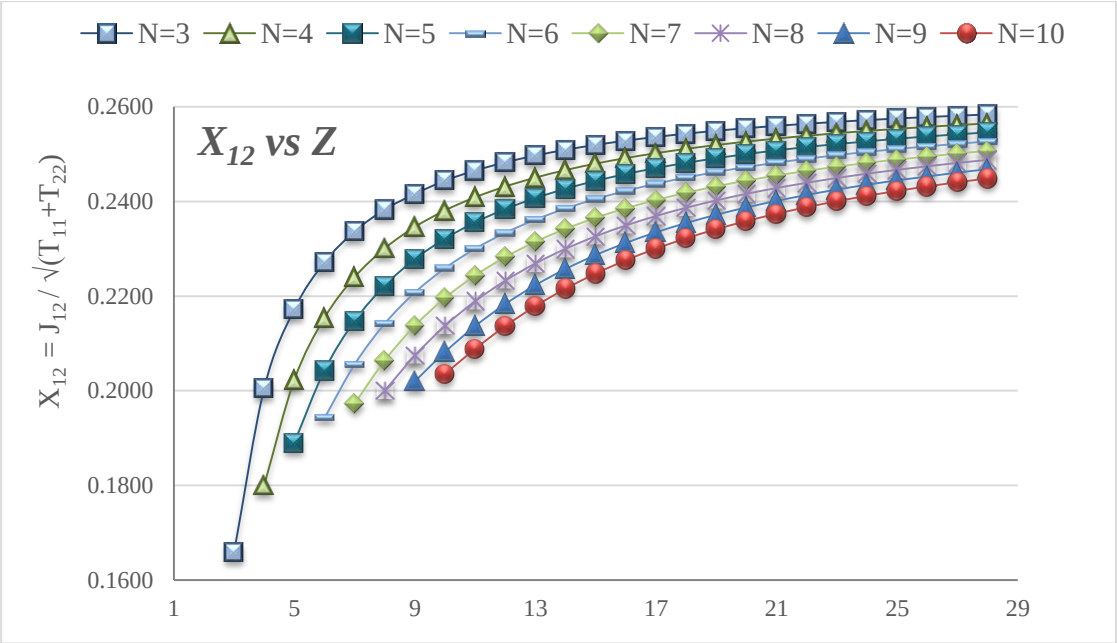


Figure 3.8c. Relationship X_{12} **vs** Z for the N=3 to N=10 isoelectronic series. (in a.u.)

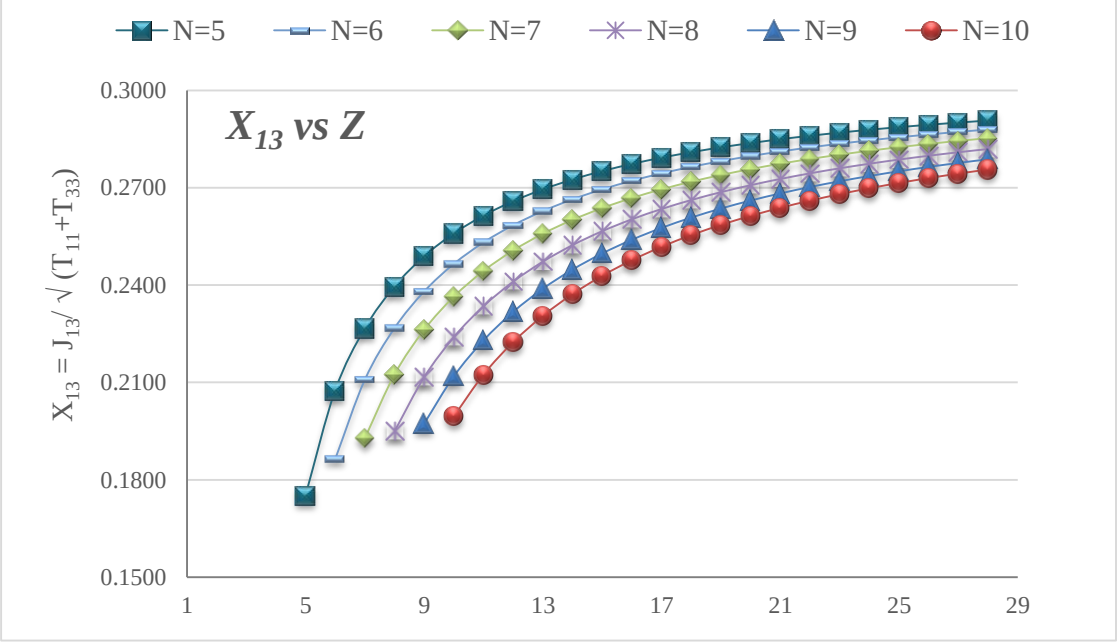


Figure 3.8d. Relationship X_{13} **vs** Z for the N=5 to N=10 isoelectronic series. (in a.u.)

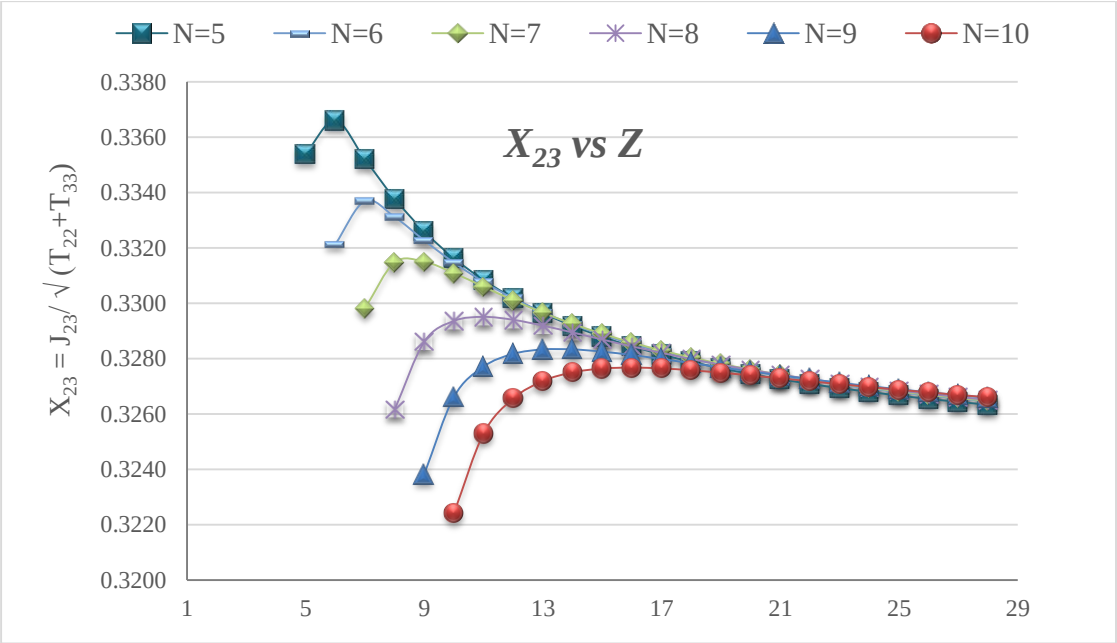


Figure 3.8e. Relationship X_{23} **vs** Z for the N=5 to N=10 isoelectronic series. (in a.u.)

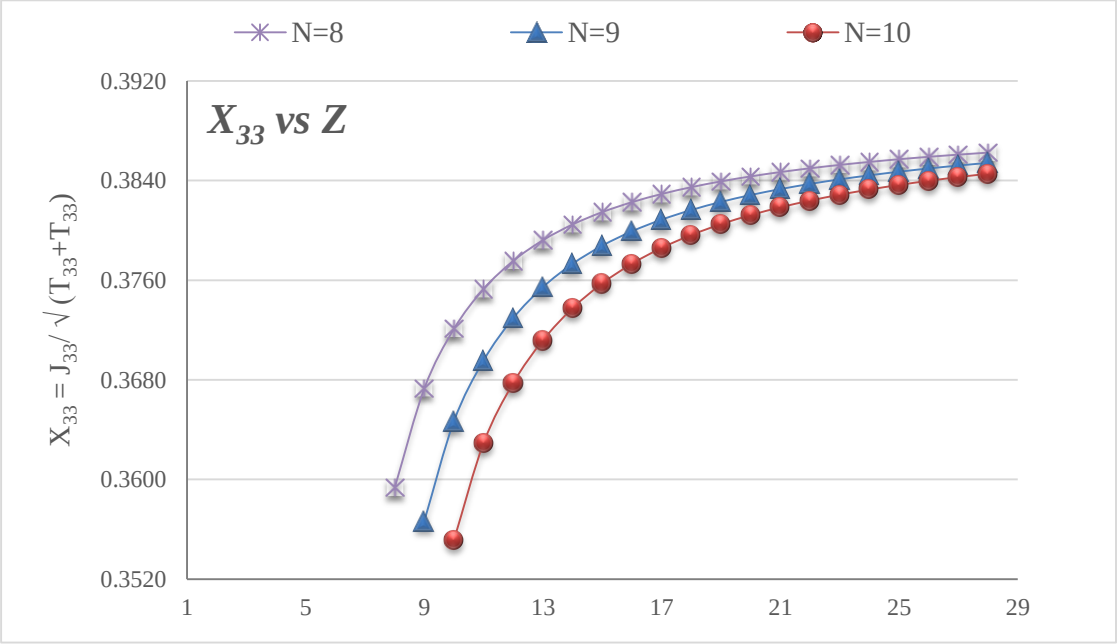


Figure 3.8f. Relationship X_{33} **vs** Z for the N=8 to N=10 isoelectronic series. (in a.u.)

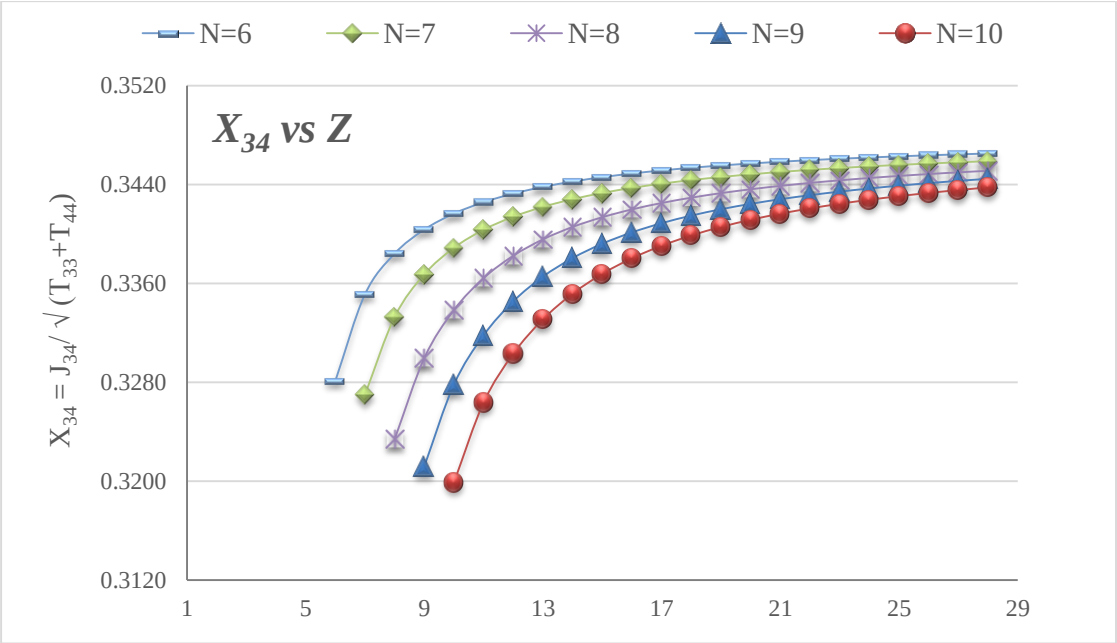


Figure 3.8g. Relationship X_{34} **vs** Z for the N=6 to N=10 isoelectronic series (in a.u.)

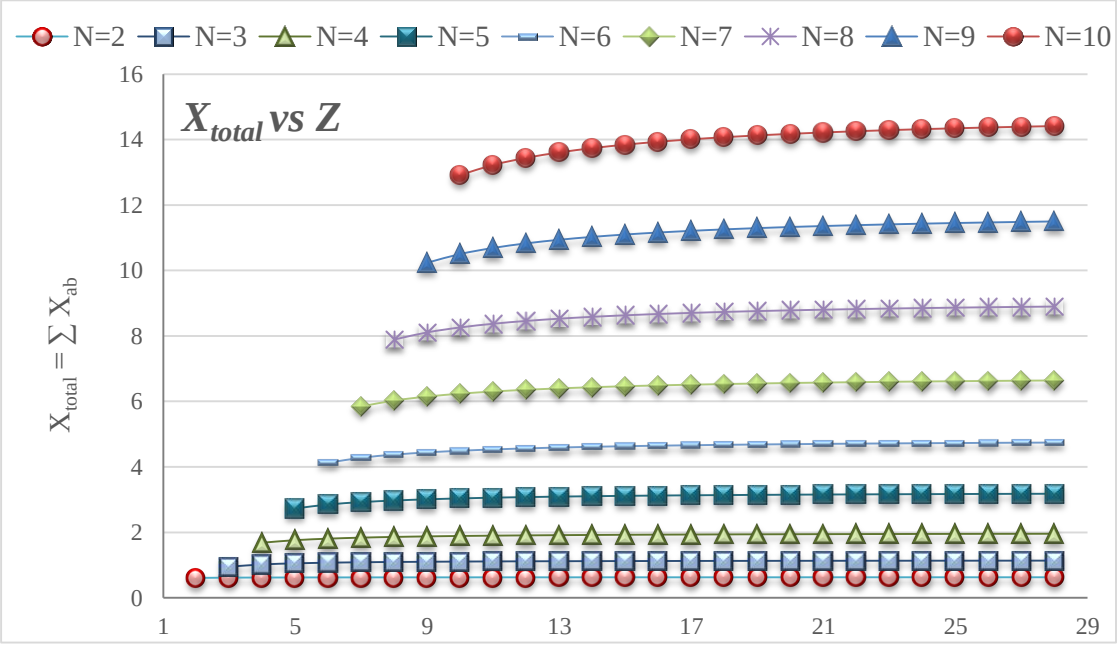


Figure 3.8h. Relationship between X_{total}, vs Z for the $N=2$ to $N=10$ isoelectronic series.

Table 3.10: Limits of E_{corr} (Hartrees) and X_{ab} (a.u.) parameters at the high Z.

	E_{corr}	X_{total}	X_{11}	X_{12}	X_{22}	X_{13}	X_{23}	X_{33_ij}	X_{33_ii}
N=2	0.0467	0.6247	0.6247						
N=3	0.0536	1.1546	0.6246	0.2650					
N=4	0.0776	1.9884	0.6250	0.2657	0.3005				
N=5	0.1186	3.2465	0.6245	0.2647	0.3006	0.3068	0.3245		
N=6	0.1732	4.8541	0.6240	0.2639	0.3006	0.3066	0.3247	0.3490	
N=7	0.2373	6.8059	0.6239	0.2630	0.3008	0.3063	0.3244	0.3483	
N=8	0.3061	9.1667	0.6233	0.2627	0.3004	0.3066	0.3249	0.3496	0.3918
N=9	0.3692	11.9775	0.6230	0.2624	0.3005	0.3087	0.3280	0.3551	0.3983
N=10	0.4270	15.2777	0.6223	0.2613	0.3007	0.3119	0.3325	0.3628	0.4077

The limits for each of the parameters above were evaluated from the Taylor expansion in 1/Z. For the *N=4*, *N=5*, and *N=6* series the limits for the correlation energy were not evaluated as the correlation energy is linear in Z.

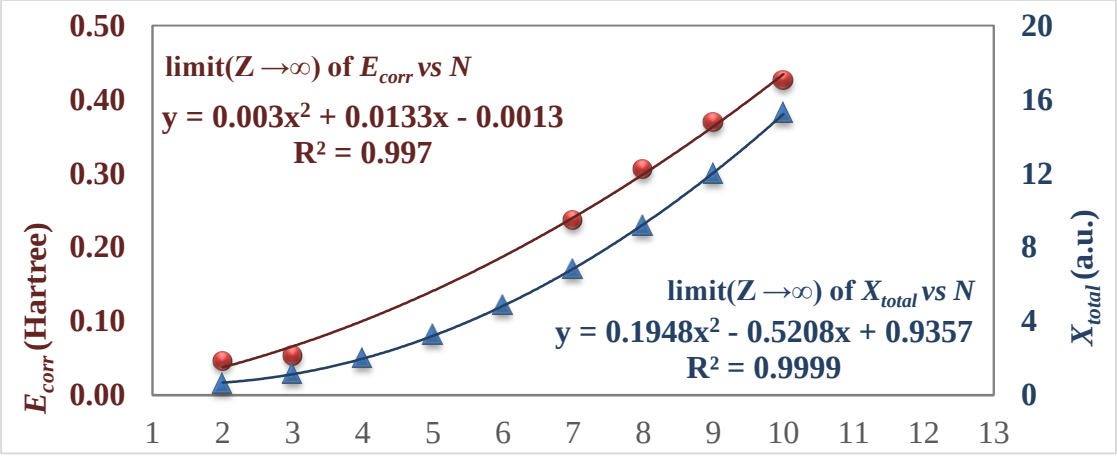


Figure 3.9. The limits at high *Z* for E_{corr} (red circles) and X_{total} (blue triangles) gradually increase with the increasing number of electrons, *N*.

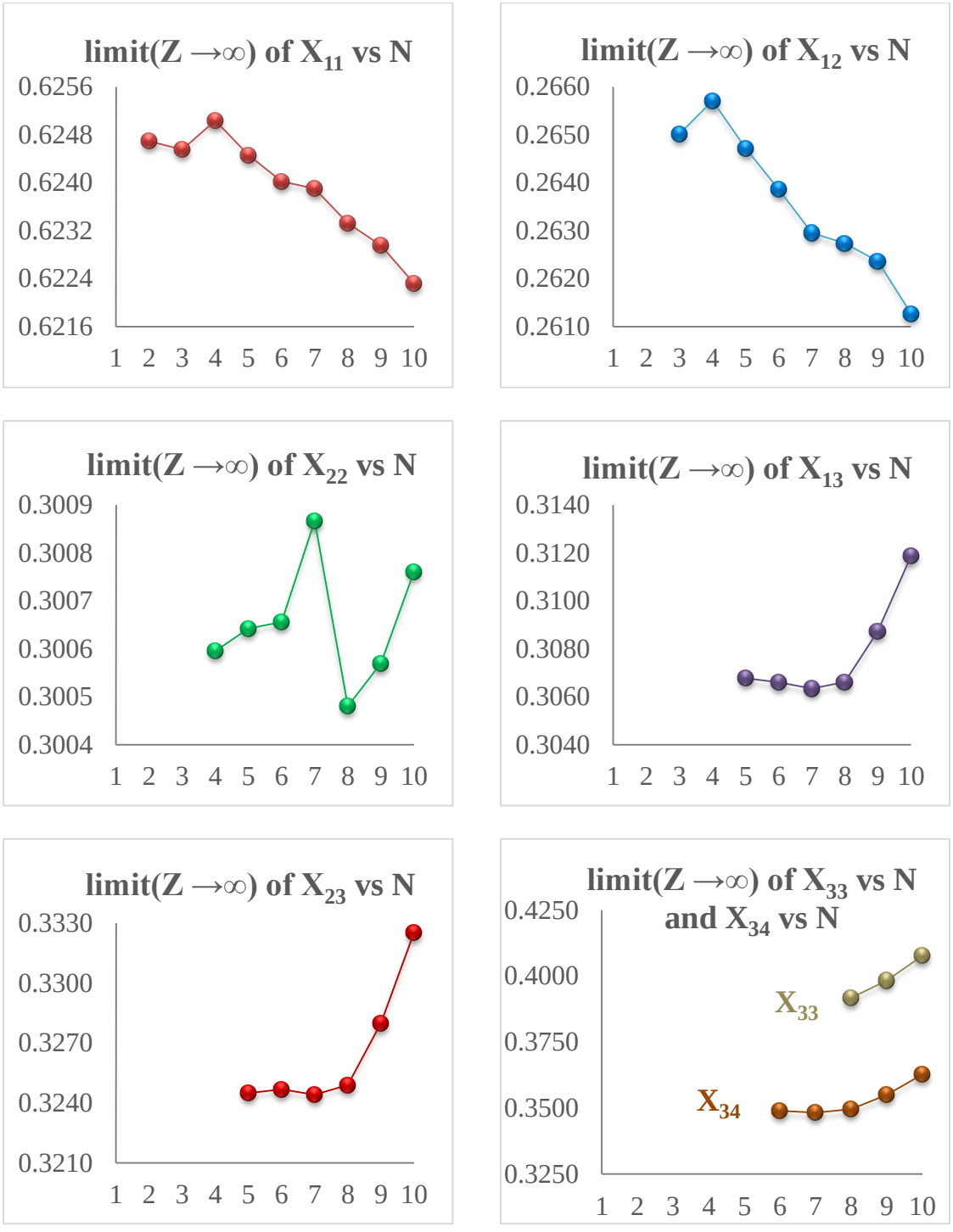


Figure 3.10. The changes in the limits at high Z for X_{ab} parameters (all given in a.u.) with the increasing number of electrons, N.

3.1.3. Electron Correlation in *N = 4, 5, 6* systems

For the atomic systems with *N=4*, *N=5*, and *N=6* the correlation energy behaves approximately as a linear function of *Z*. The linear residual term in the correlation energy expansion in *Z* arises because the linear coefficients in the expansion of the exact and Hartree-Fock energy are not equal.[28,29] As observed in the correlation energy models described in the previous paragraphs, the accuracy of fitting for the *N=4*, *N=5*, and *N=6* series is always lower than that of the other series, while the empirically determined optimized coefficients display very different behavior compared to the coefficients corresponding to the rest of the series. The modelling of the correlation energy in these systems requires a different treatment. After several trials, the simplest solution that leads to a reasonably accurate modelling of the atomic series containing 4, 5, and 6 electrons was found by adding a linear term in *Z* (*aZ+b*) to the previous models. For brevity, only the variations of the modified Model A.V for the *N=4*, *N=5*, and *N=6* atomic systems will be described further, as these capture the correlation energy behavior the best, and they also lead to the most accurate results:

Model A.VI

$$E_{corr} = C_{aa}(N)\sum_{a} X_{aa}^{1\downarrow} + C_{ab}^{1\downarrow}(N)\sum_{ab} X_{ab}^{1\downarrow} + C_{ab}^{11}(N)\sum_{ab} X_{ab}^{11} + aZ \qquad (3.26)$$

Observing the linear relationship between the Coulomb energy, *J* and exchange energy, *K* components of the total HF energy, it is possible to model the electron correlation present in the *N=4*, *N=5*, and *N=6* atomic systems including a linear function of any of these terms substituting for the nuclear charge, *Z*. It appears that the most suited linear term would include relationship with either J_{12}, K_{12} or $J_{12} - K_{12}$ terms. The

correlation model below includes a linear function in K_{12} as it leads to the best RSS values:

Model A.VII

$$E_{corr} = C_{aa}(N)\sum_{a} X_{aa}^{1\downarrow} + C_{ab}^{1\downarrow}(N)\sum_{ab} X_{ab}^{1\downarrow} + C_{ab}^{11}(N)\sum_{ab} X_{ab}^{11} + aK_{12} \qquad (3.27)$$

Additionally, it was compared whether any advantage could be gained by increasing the number of empirical coefficients in the model by fitting the correlation energy to a sum of the linear functions of each of the X_{ab} parameters separately. Initially all of the coefficients were allowed to vary for different isoelectronic systems (Model A.VIII). Afterwards, each component of the total correlation energy E_{corr_ab} would change with the changing X_{ab} parameter following the same relationship, independent of the number of electrons present in the system. While each of the X_{ab} parameters follows unique trend with respect to the increasing nuclear charge, these trends appear to be independent of N; therefore, we assume that the changes in the total correlation energy with the increasing number of electrons are due to the changes in the number of electron pairs present in the system, similar to the reasoning discussed by Alonso *et.al.*[40] with the exception of the $N=4$, $N=5$, and $N=6$ atomic systems. Figure 3.11 and Figure 3.12 illustrate this behavior, where the relationship between the correlation energy of neutral atoms and N is compared to the relationship between the number of the antiparallel electron pairs and N. The optimized coefficients for Model A.VII, Model A.VIII and Model A.IX are summarized in Table 3.11, Table 3.12 and Table 3.13, respectively, while the N relationships of the coefficients in Model A.VIII are shown in Figure 3.13.

Model A.VIII

$$E_{corr} = \sum_{a} C_{aa}^{(N)} X_{aa} + \sum_{ab} C_{ab}^{(N)} X_{ab} + c(N) K_{12} \tag{3.28}$$

Model A.IX

$$E_{corr} = \sum_{a} C_{aa} X_{aa} + \sum_{ab} C_{ab} X_{ab} + c(N) K_{12} \tag{3.29}$$

In the models above, the correlation energy is expressed as a sum of the pair correlation energies, where each electron pair is characterized by a specific value of X_{ab} parameter. There is no considerable improvement of the previous models observed by including the term for the parallel-spin electron pair correlation, where the modified X_{ab} was used, which uses (J_{ab}-K_{ab}) value, rather than the J_{ab} value. Therefore, the parallel-spin electron pair correlation was neglected in the Models A.VIII and A.IX. Finally, observing that the X_{ab} values increase with the increasing nuclear charge, and approach limiting value as $Z \rightarrow \infty$, except for the X_{22} and X_{23} parameters, it was attempted to include these in a model; however, no obvious improvements or insights have been apparent by doing so.

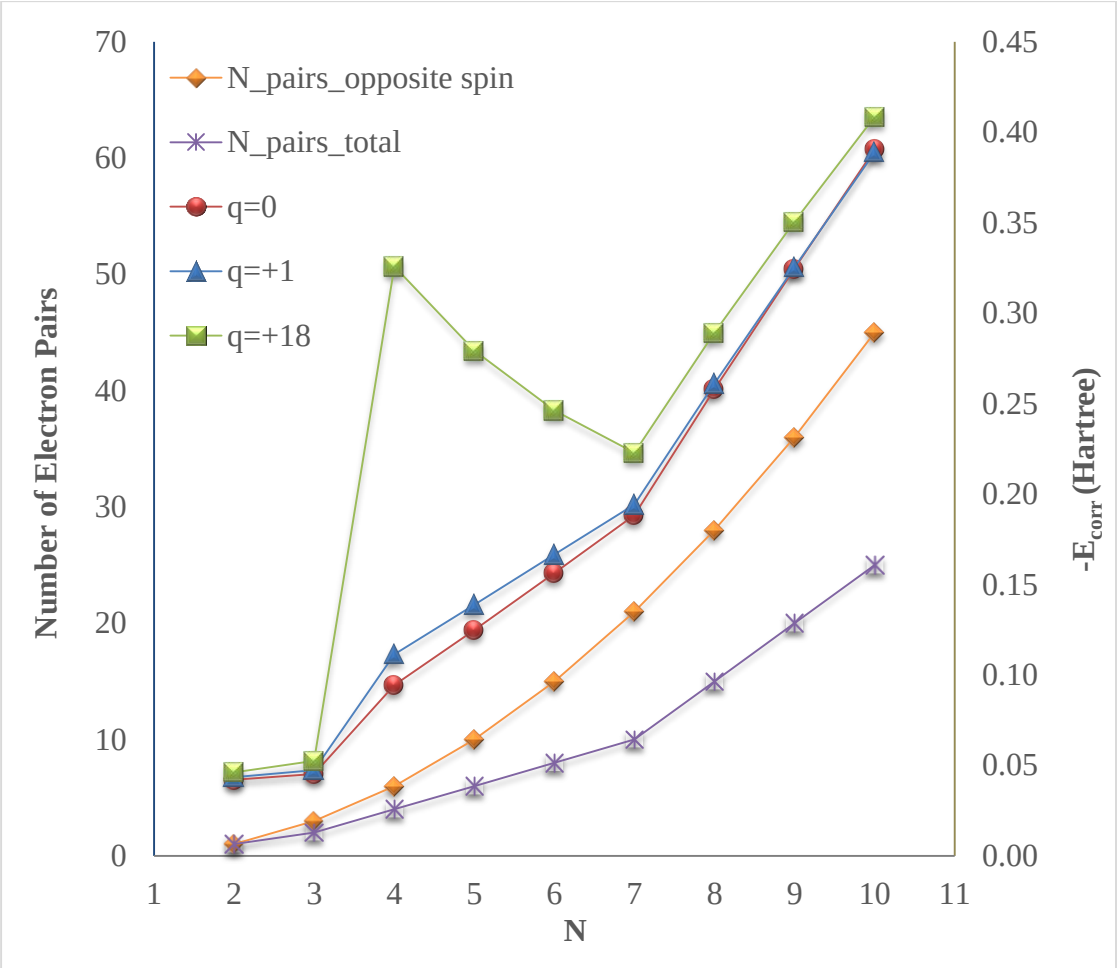


Figure 3.11. The relationship between the correlation energy of neutral atoms, and singly charged cations vs *N* is compared to the relationship between the number of the electron pairs, and the number of antiparallel electron pairs vs *N*. The curve for highly charged cations (q = +18) is included to illustrate the differences in the correlation energy behavior for the *N*=2,3 vs *N*=4,5,6 and vs *N*=7,8,9,10 series with the atomic number; specifically, small changes and close to linear dependence on *Z* (the slope E_{corr} vs *N* is almost constant with the increasing charge of an ion (and therefore with the increasing nuclear charge) for the *N*=2,3 and *N*=7,8,9,10 series, while the slope changes drastically for the *N*=4,5,6 series.

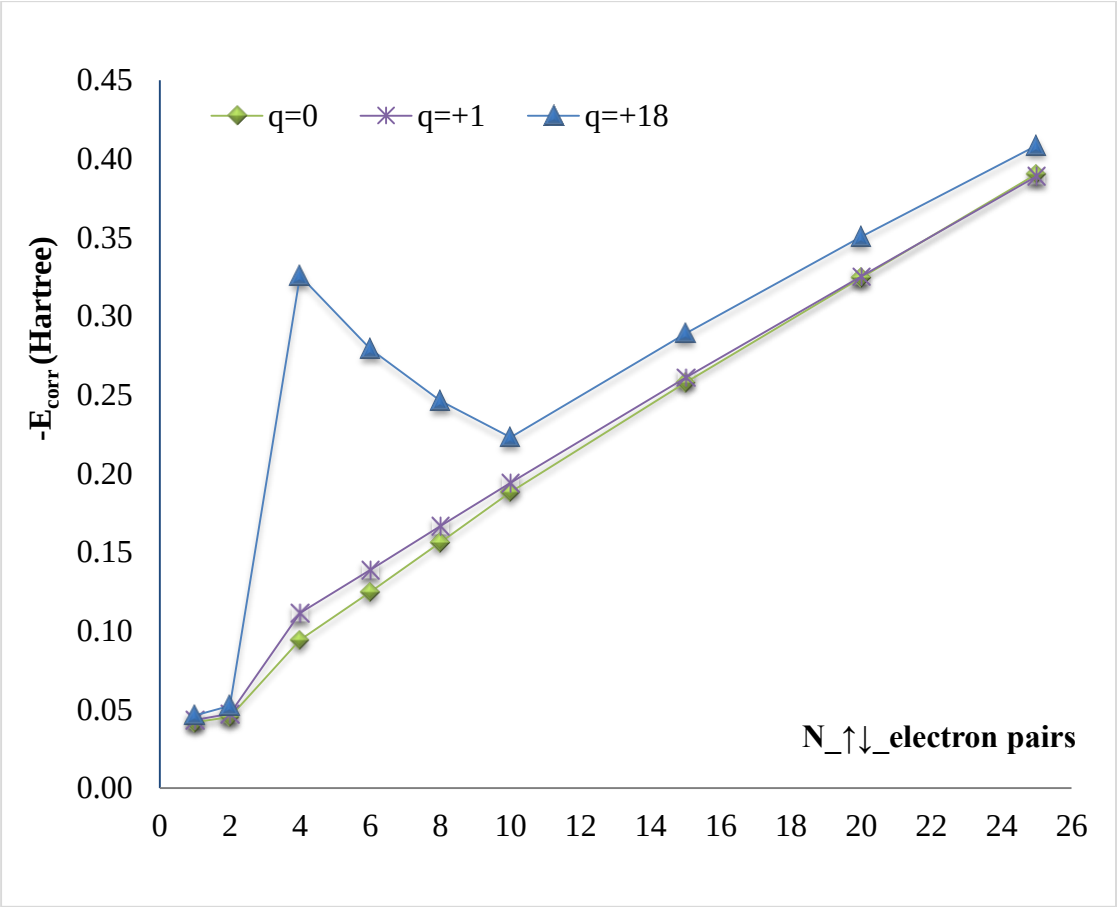


Figure 3.12. The relationship between the correlation energy of neutral atoms, and singly charged cations vs number of antiparallel electron pairs. The curve for highly charged cations (q=+18) is included to illustrate the differences in the correlation energy behavior for the *N=4,5,6* isoelectronic series.

Table 3.11: The optimized parameters for Model A.VII. (in a.u.)

	$C_{aa\_\downarrow\uparrow}$	$C_{ab\_\downarrow\uparrow}$	$C_{ab\_\uparrow\uparrow}$	c	$RSS^{Model\ A.VII}$
N=2	0.0734	-	-	-	$1.43E^{-5}$
N=3	0.0756	0.4679	-0.4968	0.0004	$4.24E^{-9}$
N=4	0.0439	0.8988	-0.7252	0.5357	$8.68E^{-9}$
N=5	0.0149	0.9219	-0.9099	0.3164	$1.91E^{-7}$
N=6	0.0856	0.5483	-0.4568	0.1435	$1.23E^{-8}$
N=7	0.2020	0.4317	-0.3217	0.0037	$2.13E^{-9}$
N=8	0.2994	1.7987	-1.8705	0.0146	$1.07E^{-5}$
N=9	0.1781	-2.5830	2.8999	0.0229	$3.91E^{-7}$
N=10	0.2211	-2.6685	2.9659	0.0237	$1.88E^{-7}$

Table 3.12: The optimized parameters for Model A.VIII. (in a.u.)

	C_{aa}	C_{ab}	c	$RSS^{Model\ A.VIII}$
N=2	0.0734	-	-	$1.43E^{-5}$
N=3	0.0549	0.0340	0.0018	$3.69E^{-7}$
N=4	0.0261	0.0763	0.5380	$4.05E^{-7}$
N=5	-0.0019	0.0640	0.3217	$7.25E^{-7}$
N=6	-0.0158	0.0513	0.1507	$1.26E^{-6}$
N=7	0.0025	0.0375	0.0165	$3.17E^{-6}$
N=8	0.0884	0.0211	0.0299	$1.14E^{-5}$
N=9	0.17362	0.0036	0.0443	$2.06E^{-5}$
N=10	0.2814	-0.0167	0.0630	$2.79E^{-5}$

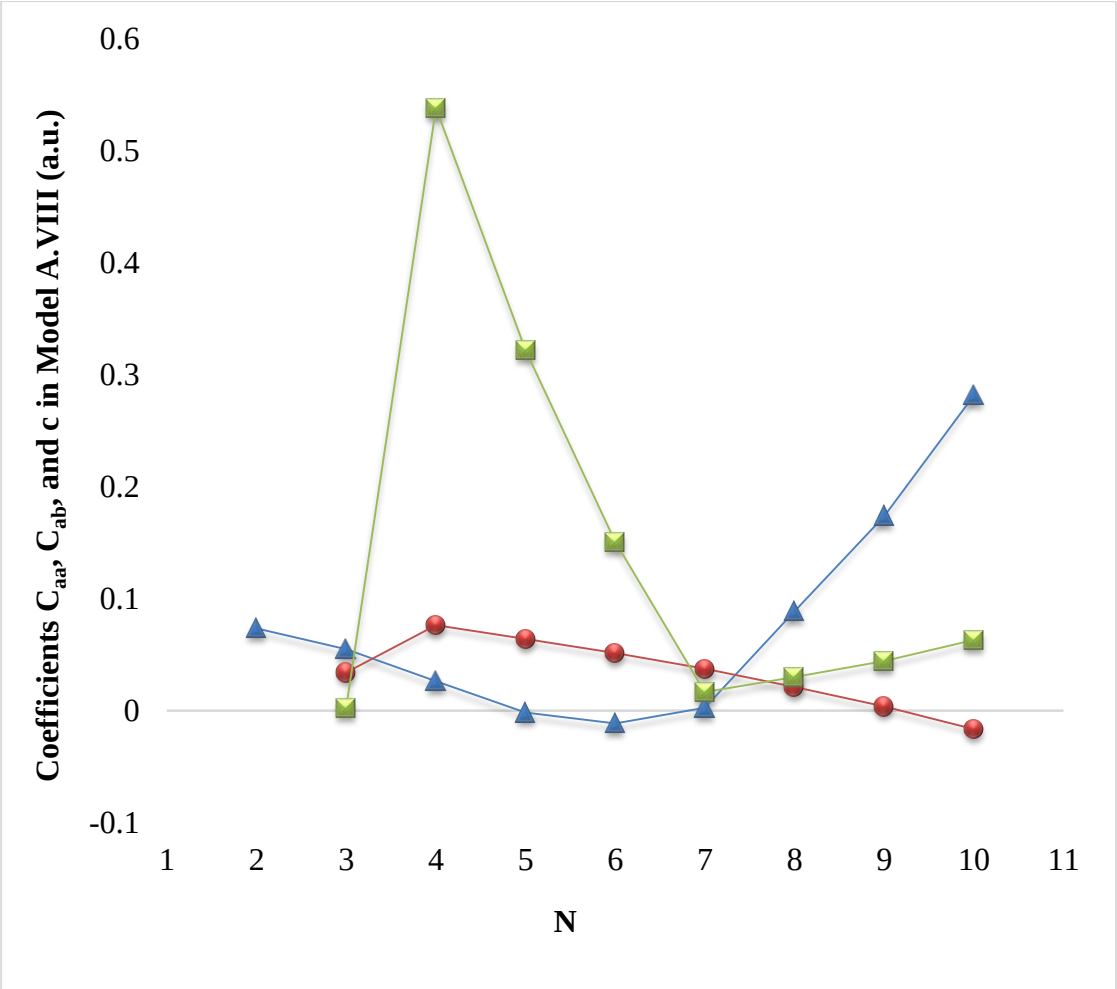


Figure 3.13. The relationship between the coefficients C_{aa} (blue triangles), C_{ab} (red circles) and c (green squares) of Model A.VIII vs *N*.

Table 3.13: The optimized parameters for Model A.IX. (in a.u.)

	c	C_{11}	C_{12}	C_{22}	$RSS^{Model\ A.IX}$
N=2	-	0.0734	-	-	$1.43E^{-5}$
N=3	0.0018	0.0549	0.0681	-	$3.69E^{-7}$
N=4	0.5358	-0.3179	0.5851	0.4990	$7.65E^{-9}$
N=5	0.3188	0.1360	0.5439	-0.4150	$6.91E^{-9}$
N=6	0.1436	0.6353	-0.6792	0.1003	$1.58E^{-10}$
N=7	0.0036	-3.6424	1.9978	7.2658	$1.09E^{-9}$
N=8	0.0021	3.0461	-1.2756	-3.9623	$1.36E^{-10}$
N=9	0.0019	1.2640	-0.1455	0.1583	$1.26E^{-10}$
N=10	0.0047	7.6498	-4.2093	-8.4183	$1.07E^{-10}$
	C_{13}	C_{23}	$C_{34,35,45}$	$C_{33,44,55}$	
N=5	-0.1224	0.2532	-	-	
N=6	1.1539	0.8655	-	-	
N=7	1.2732	0.6828	-2.3504	-	
N=8	0.4886	0.1360	-1.2280	0.4186	
N=9	-0.2542	-5.5731	16.2188	-10.7552	
N=10	0.9944	-0.5367	-32.7200	27.0478	

3.2. Modelling of Molecular Systems

3.2.1. Simple Linear Relationships

The correlation energies of neutral and slightly charged positive and negative ions were linked to the number of the electrons and the antiparallel spin electron pairs in the same main shell, while the inter-shell correlation energies are assumed minor, and their effect is approximately included within a single optimized parameter, that averages the pairing energy. The relationship between the atomic correlation energies and the number of the opposite-spin electron pairs has been extended to include the orbital dependency of pairing energies in the later work of Alonso *et. al*.[41]

A similar modeling was applied to molecular systems by fitting the correlation energies of 56 simple molecules as a linear function of N and $N_{\uparrow\downarrow pairs}$; however, the quadratic relationship between the total correlation energy and the number of the electron pairs with the opposite spin in the system gives much better fit:

Model M.I

$$E_{corr} = C_I N + c_I \tag{3.30}$$

Model M.II

$$E_{corr} = C_{II}\sqrt{N_{\uparrow\downarrow pairs}} + c_{II} \tag{3.31}$$

These relationships are illustrated in Figure 3.14, while optimized coefficients and RSS values are listed in Table 3.14.

Models describing the relationships between the correlation energy and size of the electron pair in the atomic series have been extended and applied to molecular systems, where it has been shown that the large amount of the missing energy could be

approximated from the size of an electron pair associated with a localized molecular orbital (LMO), $\langle r^2 \rangle_{R_a}$. The size of a localized molecular orbital *a* has been related to the orbital energy, ϵ_a. It is reasonable to assume that the correlation between the electrons should increase as the volume occupied by an electron pair decreases; in other words, the closer the electrons are to each other, the more correlated their motion is. Fröman proposed a semi-empirical formula using the mean value of the inter-electronic distance, which is related to the size of an electron pair, and proposed an inverse relationship between molecular correlation energy the average inter-electronic distance. Furthermore, the average distance between the electrons is related to the inverse of the Coulomb repulsion energy corresponding to the electron pair, as has been discussed by Hollett and Poirier.[34] These ideas have been extended by fitting the molecular correlation energy as a function of the total Coulomb energy. It has been found that much better fit is obtained by relating the square root of the total Coulomb energy to the total correlation energy, and so the quadratic relationship is discussed here, rather than the linear function. The results of the fitting are summarized in Table 3.14.

Model M.III

$$E_{corr} = C_{III} \sqrt{\sum_{ab} J_{ab}} + c_{III} \tag{3.32}$$

Additionally, an extension of the atomic correlation energy models involving the relationship between the electron pair correlation energy and the ratio of the Coulomb and the kinetic energies to the molecular systems was considered, where the fitting parameters were defined as:

$$X_{SUM} = \sum_{ab} X_{ab} = \sum_{ab} \frac{J_{ab}}{\sqrt{(T_{aa} + T_{bb})}} \tag{3.33}$$

$$X_{total} = \sum_{ab} J_{ab} \; / \sqrt{\sum_{a} T_{aa}} \tag{3.34}$$

The linear behavior of the parameters $\sum X_{ab}$ and X_{total} with the increasing N is similar to that of the total correlation energy (Figure 3.15); therefore, the relationship between the molecular correlation energy and the parameters $\sum X_{ab}$ and X_{total} in the way analogous to the atomic systems was considered. The total correlation energy was fitted as a linear function of the sum of the parameters $\sum X_{ab}$ (Model M.IV), where the sum includes all the electron pairs of the molecular system. However, the fitting of the correlation energy as a linear function of a parameter X_{total} gives similar results with comparable accuracy, while it simplifies the model (Model M.V). The results are summarized and compared to the previous models in Table 3.14.

Model M.IV

$$E_{corr} = C_{IV} X_{SUM} + c_{IV} \tag{3.35}$$

Model M.V

$$E_{corr} = C_{V} X_{total} + c_{V} \tag{3.36}$$

While the above models are reasonably accurate considering their simplicity, there is no systematic trend observed with regards to the error associated with these models, and it is not possible to predict whether the calculated correlation energy would be below or above the actual value for a molecule outside of the set.

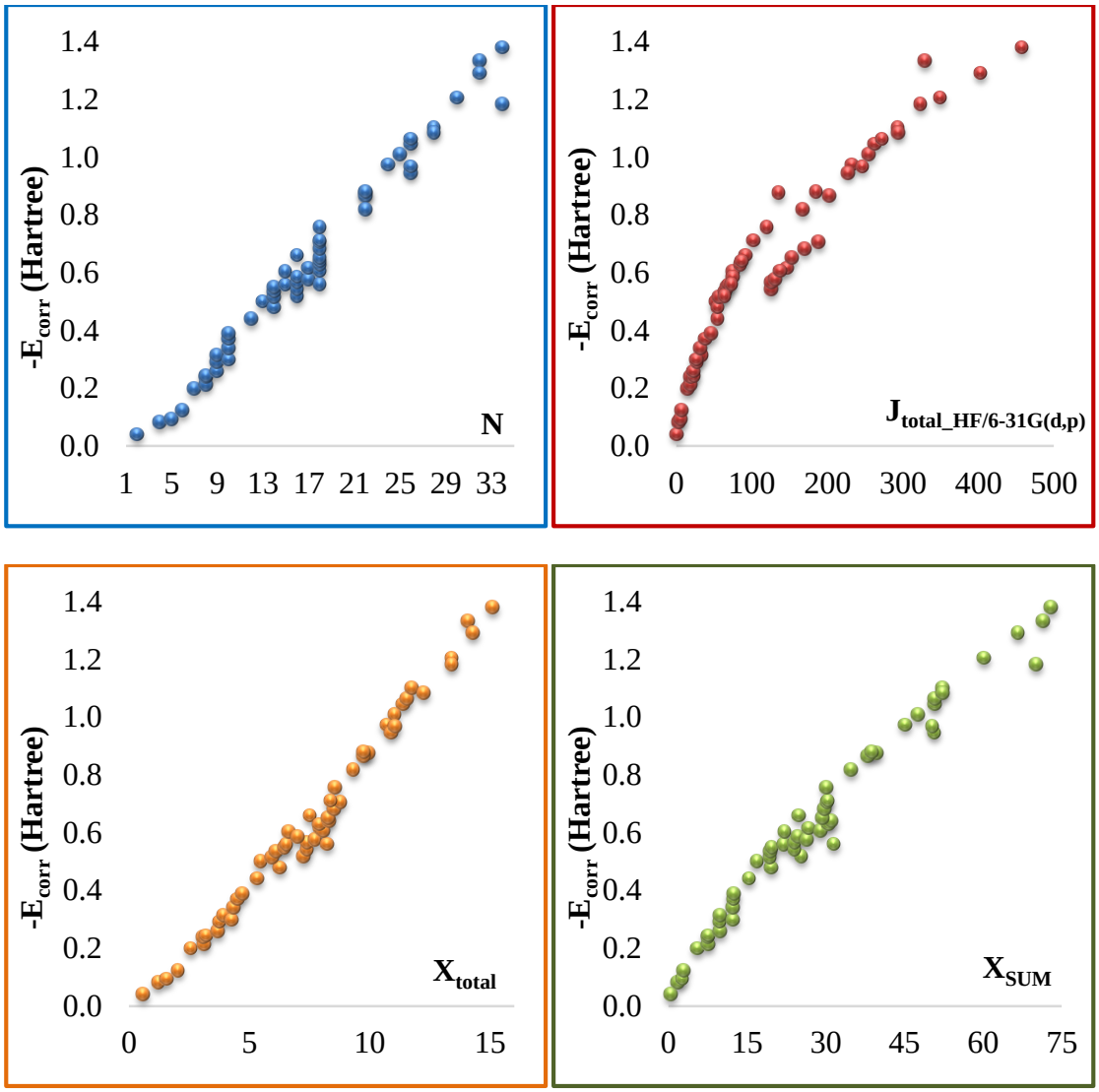


Figure 3.14. The relationship between the molecular correlation energy and the number of electrons present in the system; compared to the relationships vs Coulomb energy, and the ratio of Coulomb energy and square root of the kinetic energy.

Table 3.14: The optimized parameters for Models M.I-M.V. (in a.u.)

	Parameter	C_i	c_i	R^2
Model M.I	N	0.0458	-0.0963	0.9770
Model M.II	$(N_{\downarrow\uparrow pairs})^{1/2}$	0.0915	-0.0936	0.9770
Model M.III	$(\sum J_{ab})^{1/2}$	0.0712	-0.0449	0.9430
Model M.IV	$\sum X_{ab} = \sum (J_{ab}/(T_{aa}+T_{bb})^{1/2})$	0.1024	-0.0834	0.9747
Model M.V	$X_{total} = \sum J_{ab}/(\sum T_{aa})^{1/2}$	0.0192	0.1377	0.9711

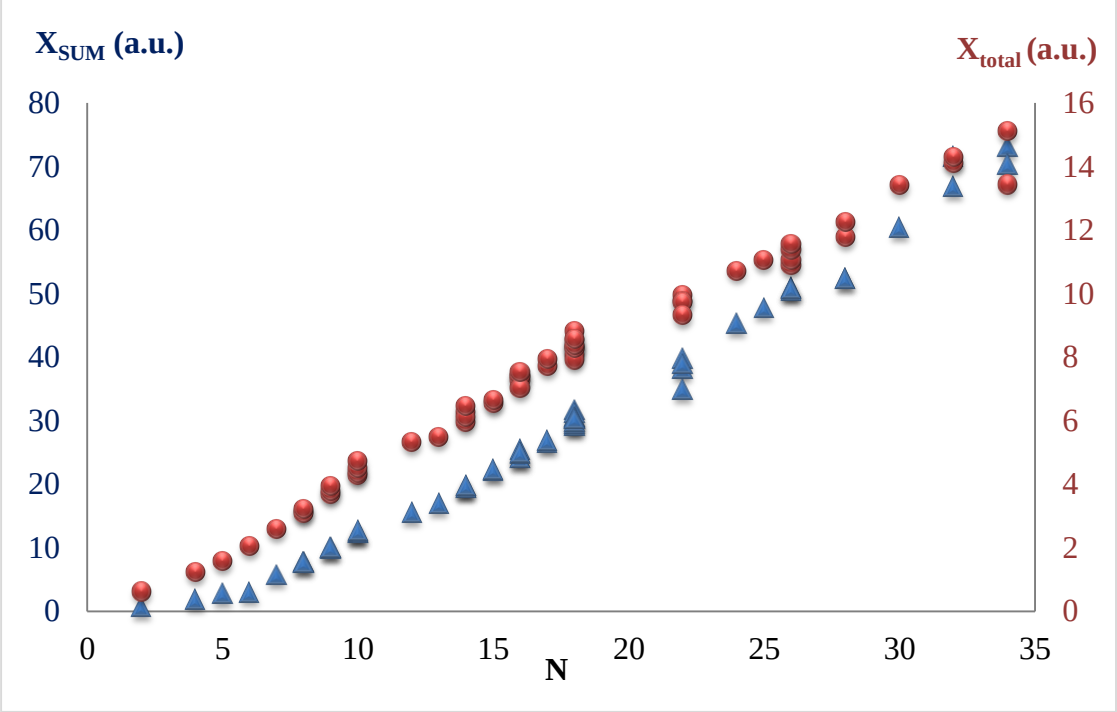


Figure 3.15. The relationship between *N* and parameters X_{SUM} from equation 3.33 (blue traingles, primary axes) and X_{total} from equation 3.34 (red circles, secondary axes).

However, some interesting insights are observed from the above relationships, which might be helpful in the development of more accurate molecular correlation energy models. More precisely, the molecules studied were arranged into several groups, or subsets, with respect to the correlation energy behavior with the increasing number of electrons, and also with respect to the increasing value of the nuclear charge of the atoms constituting a molecular system. By modelling the correlation energies of a group of the molecules sharing similar molecular structure only, it is possible to obtain more accurate fittings; at the same time, comparing the similarities and differences between the correlation models corresponding to different groups it might be possible to acquire a better understanding of the molecular correlation behavior in general. It was found that four distinct molecular groups suit the partitioning of the molecular systems with respect to the correlation energy behavior best: in the first group the focus is only on the diatomic homonuclear molecular systems, the second group contains the heteronuclear molecules not containing hydrogen atom, in the third group the molecules containing only a single atom other than hydrogen were explored, while the fourth group contains all other molecules in the set: the hydrides containing two atoms, same or different, other than hydrogen. Figure 3.16 illustrates these four distinct groups within our molecular set, based on their structure, which is reflected in their correlation energy behavior with the increasing number of electrons and the increasing nuclear charge of the constituent atoms. Atomic correlation energies of the constituent atoms are included in the plot for comparison. At the same time, notice that for each of the groups of molecules there is a clear separation in the curve between the molecules containing first row elements, with

or without hydrogens, and the molecules containing at least one element of the second row of the periodic table. These differences likely arise from the increasing number of core electrons, and the increasing nuclear charge is expected to play an important role as the core electrons are moving closer to a nucleus.

Similarities are also observed with regards to a trend in the correlation energy relationships vs $\sum X_{ab}$ and X_{total} between atomic and molecular systems, while the linear relationship vs X_{total}, is surprisingly much better fit than the linear relationship vs $\sum X_{ab}$. Models M.IV and M.V were therefore slightly revised to fit a group of the molecules that share similar molecular structure to a linear function of the above parameters, instead of fitting all molecular systems together. By adjusting the empirical coefficients to obtain more accurate fit, we hope to gain better reproducibility of a model when applied to the wider range of molecular systems. Figure 3.17 illustrates these adjustments, and the specific coefficients corresponding to each group are summarized in Table 3.15. It was found that a better fit is obtained by modelling the correlation energy as a power function of the parameter $\sum X_{ab}$ rather than a linear function; therefore, the coefficients corresponding to a power function are also included for comparison.

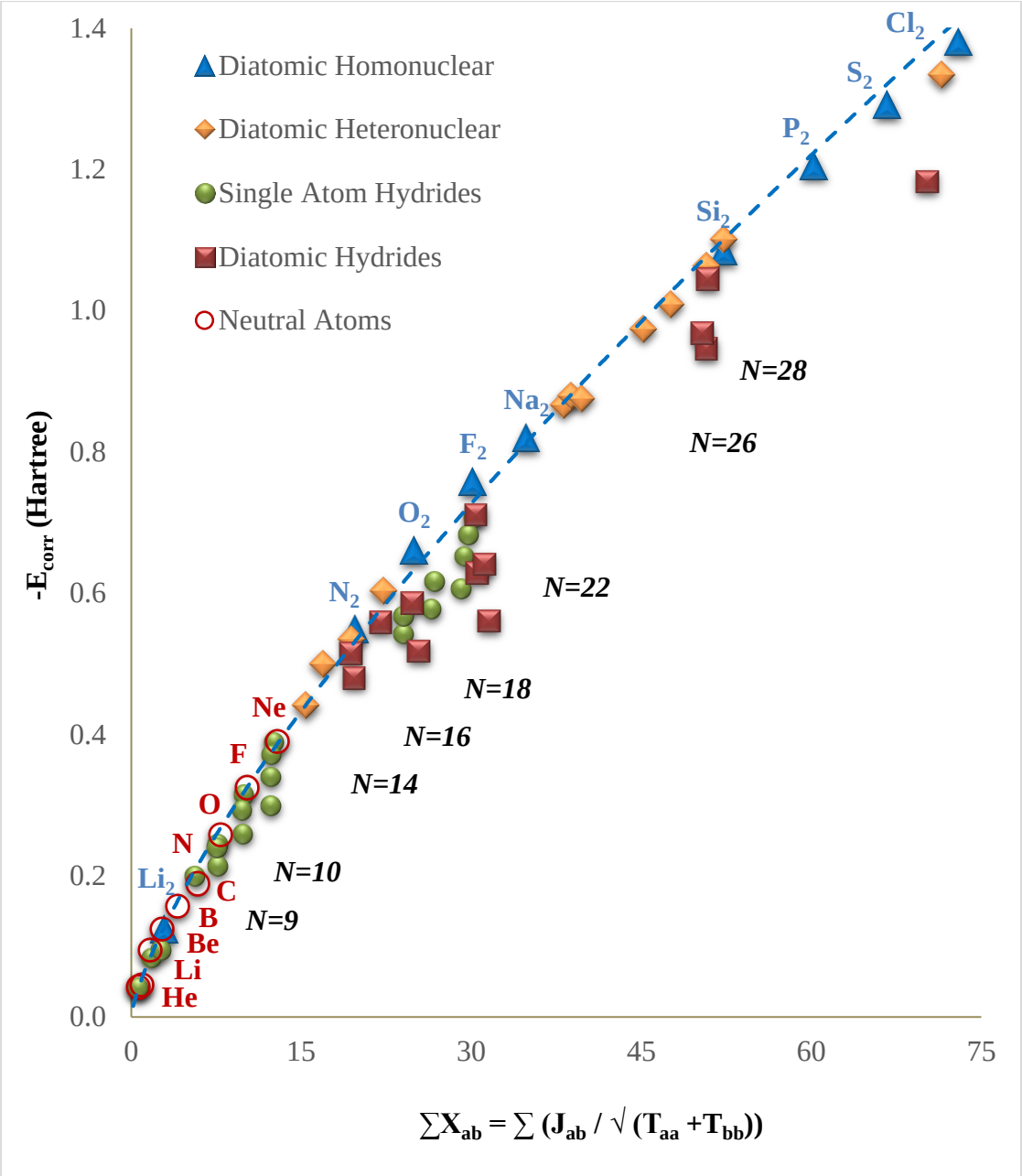
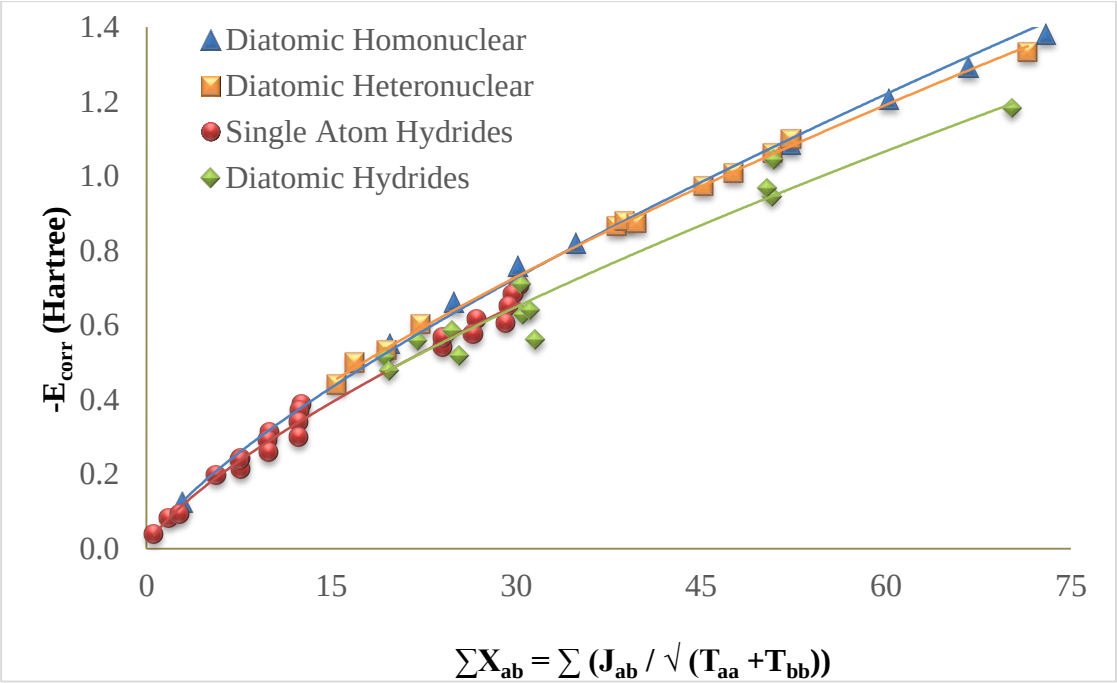


Figure 3.16. The molecular correlation energy vs $\sum X_{ab}$; illustrating four distinct groups within the set of 56 small molecular systems, based on their structure, which is reflected in their correlation energy behavior with the increasing number of electrons and the increasing nuclear charge of the constituent atoms.



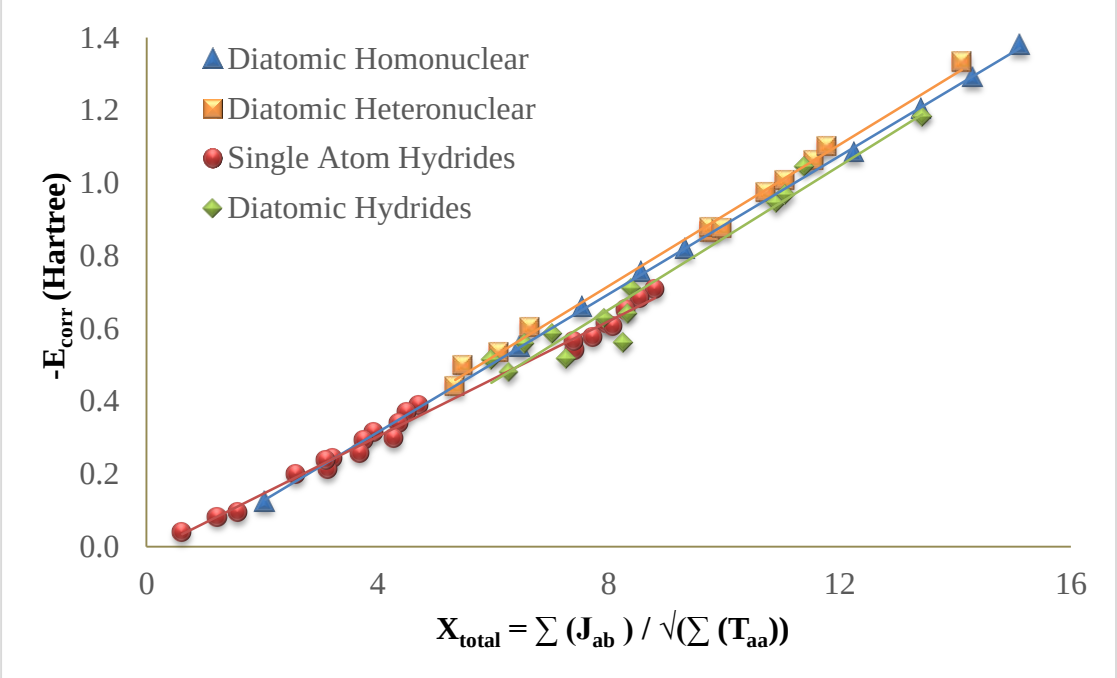


Figure 3.17. The relationship between the molecular correlation energy and the ratio of Coulomb energy and squared root of the kinetic energy for the selected molecular groups.

Table 3.15: The optimized parameters for the modified Model M.IV ($\sum X_{ab}$ relationship), and for modified Model M.V (X_{total} relationship) for the selected groups of the molecular systems. (all given in a.u.)

		C_i	c_i	R^2
Model M.IV$_m$ $E_{corr} = C_{IVm} \sum X_{ab} + c_{IVm}$	AA	0.0169	0.1870	0.9818
	A_1A_2	0.0161	0.2325	0.9923
	AH_n	0.0201	0.0743	0.9790
	$A_1A_2H_n$	0.0147	0.2019	0.9487
Model M.IV$_n$ $E_{corr} = C_{IVn} (\sum X_{ab})^{c_{IVn}}$	AA	0.0572	0.7477	0.9985
	A_1A_2	0.0659	0.7071	0.9976
	AH_n	0.0530	0.7394	0.9898
	$A_1A_2H_n$	0.0568	0.7166	0.9293
Model M.V$_m$ $E_{corr} = C_{Vm}\ X_{total} + c_{Vm}$	AA	0.0950	-0.0654	0.9996
	A_1A_2	0.0973	-0.0613	0.9954
	AH_n	0.0793	-0.0144	0.9924
	$A_1A_2H_n$	0.0990	-0.1404	0.9526

AA symbolizes the homonuclear diatomic molecules with no hydrogens. A_1A_2 denotes the heteronuclear diatomic molecules with no hydrogens. AH_n symbolizes molecules containing only a single atom of the first or second row of the periodic table other than hydrogen (monoatomic hydrides), while $A_1A_2H_n$ represents molecules containing at least two atoms other than hydrogens (diatomic hydrides).

3.3. Summary: Correlation Energy of the Atomic and Molecular Systems

The performance of the correlation energy models for the atomic systems has been assessed using the average deviation (AD), mean average deviation (MAD) values, and the standard deviation (STD) statistical values. These, along with the RSS values corresponding to each model, are summarized for a few representative atomic correlation models in Table 3.16. Similarly, the performance of the molecular correlation models was evaluated, and also compared to the performance of the higher level of theory correlated methods; specifically, MP4(FULL), CISD(T), and CCSD(T) and the results are listed in Table 3.17.

The atomic correlation energy models presented here can successfully account for the missing correlation energy in the atomic isoelectronic series quite well, and are within chemical accuracy. We are confident that these models would be able to predict reliable correlation energies for the atomic and cationic systems containing 2-10 electrons. However, the relationship of correlation energy with respect to *N* does not follow a simple function; therefore, while we are able to construct a successful model using the available correlation energy data, further work is needed to develop a reliable models for the N>10 isoelectronic systems. The most difficult part in the correlation energy modelling of the atomic systems is to correctly describe the correlation energy behavior for *N=4*, *N=5*, and *N=6* series simultaneously and in relation with the rest of the *N* series. Despite the systematic increase in the correlation energy with the increasing number of electrons from *N=7* to *N=10*, it is expected that a certain deviation from the gradual increase will be observed in the correlation models for higher *N*, similar to the

four electron series. It is estimated that periodicity in the pattern will also emerge, reflecting the periodicity in the filling of the atomic orbitals; although, it is not expected to be as extreme as for the *N=4* atomic systems.

The performance of the molecular correlation models is remarkably good, considering their computational simplicity, especially when compared to the higher level correlated computational methods, such as CI or CC. The calculated MAD values for the selected models are smaller than those for the high level correlated methods; meaning the predicted electron correlation energies deviate from the actual values less. Figure 3.19 and Figure 3.20 illustrate these results as they also point out different trends demonstrated by our models, (which are behaving similar to each other), compared to the trends demonstrated by the other correlated methods. The similar trends observed here are likely due to the approach of treating the correlation energy problem by the corresponding theoretical method. However, the basis set used to calculate the correlated energies using MP4, CI, and CC levels was small; therefore, the accuracy of the correlated methods is greatly affected by the basis set incompleteness error, much more than those of HF calculations. Nevertheless, considering the simplicity of these models, their computational efficiency would still be advantageous over the other methods. The main drawback of our models though would be their limited applicability to a wider range of molecules that do not fall into the four group categories described here. Further work is needed to extend the generality of the suggested models.

Table 3.16: Average Deviation (AD) and Mean Average Deviation (MAD) for selected atomic correlation energy models.

	Average RSS	STD	AD	MAD
Model A.II	$1.31E^{-4}$	0.0049	0.0017	0.0018
Model A.III$_a$	$8.41E^{-5}$	0.0021	0.0012	0.0011
Model A.III$_b$	$5.63E^{-6}$	0.0021	0.0014	0.0014
Model A.IV	$8.07E^{-3}$	0.0188	0.0091	0.0091
Model A.VIII	$1.31E^{-4}$	0.0007	0.0004	0.0004
Model A.IX	$8.90E^{-6}$	0.0003	0.0002	0.0002

The error for each model was calculated as a difference between the exact energy and the total energy calculated using 6-31G(d,p) basis set. Therefore, the error is not strictly just the missing correlation energy, but it also includes the basis set incompleteness error. (STD, AD, MAD are all given in Hartrees.)

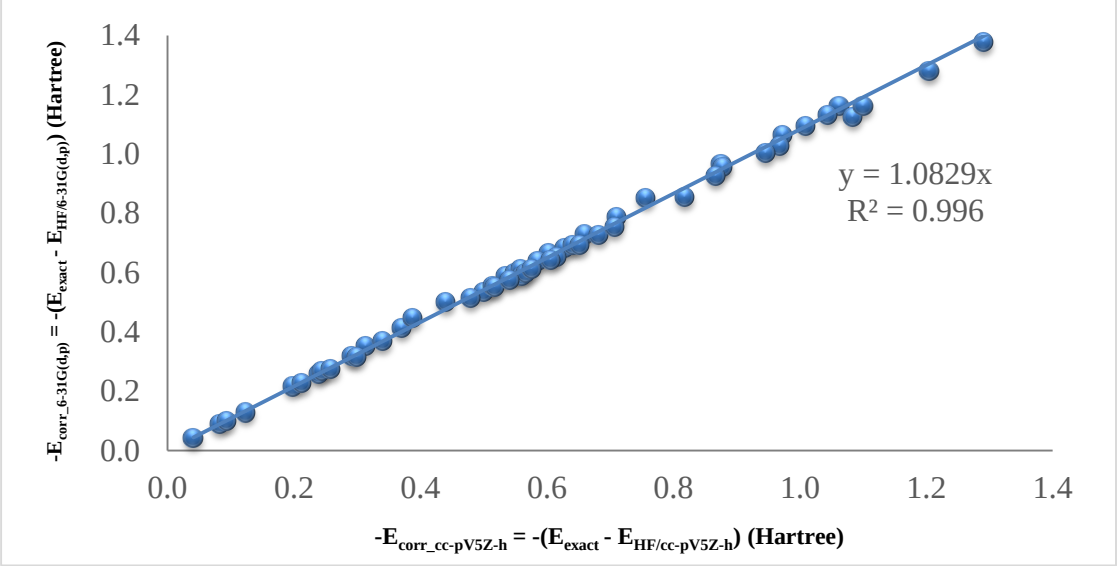


Figure 3.18. The linear relationship between E_{corr_V5Z} and $E_{corr\_6\text{-}31G(d,p)}$, both calculated as a difference between the exact energy and HF energy according to Löwdin's definition.

Table 3.17: Average Deviation (AD), Mean Average Deviation (MAD), and Standard Deviation (STD) for the molecular correlation energy models.

	AD	***MAD***	***STD***
MP4SDTQ(FULL)	0.446	0.258	0.307
QCISD(T)	0.455	0.262	0.312
CCSD(T)	0.455	0.262	0.312
Model M.I	0.045	0.045	0.056
Model M.II	0.045	0.045	0.088
Model M.III	0.063	0.063	0.059
Model M.IV	0.052	0.052	0.063
Model M.IV_m	0.059	0.038	0.050
Model M.V	0.047	0.047	0.059
Model M.V_m	0.058	0.037	0.050

The error for each model was calculated as a difference between the exact energy and the total energy calculated using the correlated method with 6-31G(d,p) basis set. Therefore, the error is not strictly just the missing correlation energy, but it also includes the basis set incompleteness error. Although it is shown that the HF energy for the selected molecules calculated using 6-31G(d,p) basis is almost linear with the HF energy calculated using large cc-p-V5Z basis, it is known that the effect of the basis set size when used with higher levels of theory like CI or CC is much stronger, and the larger basis usually improves the calculations greatly. (This work is to be completed in the near future.) (All data in Hartrees.)

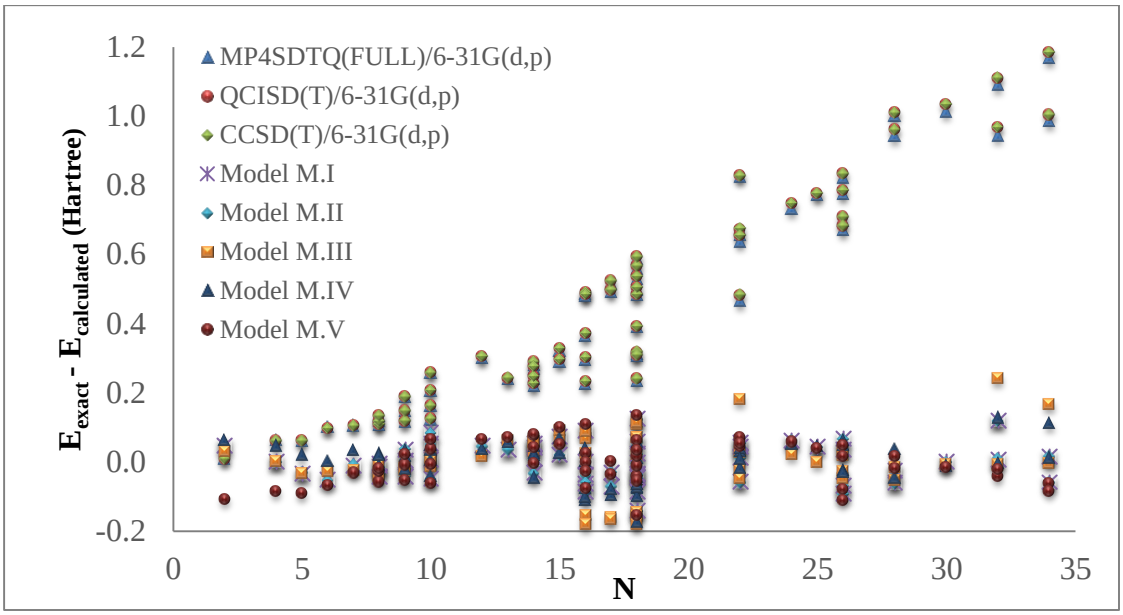


Figure 3.19. The deviation of the calculated energy from the exact non-relativistic energy vs. *N*.

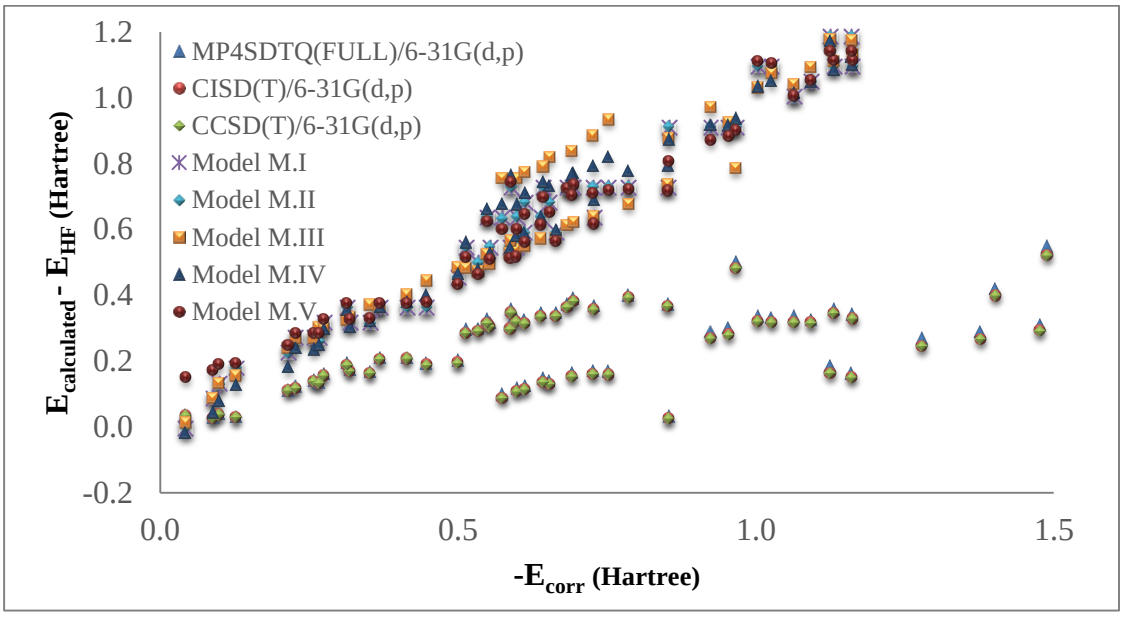


Figure 3.20. The difference between the calculated model or correlated method energy and the Hartree-Fock energy, compared to the actual correlation energy.

4. Conclusions and Future Work

4.1. Atomic Models

The electron correlation problem continues to be one of the most challenging computational chemistry problems. Although the Hartree-Fock approximation is generally successful in predicting approximately 99% of the total non-relativistic energy, the remaining 1% is extremely important in determination of the accurate molecular properties. Without including the electron correlation energy, molecular properties such as bond energies, equilibrium geometries, dipole moments, or reaction kinetics cannot be determined accurately for chemical systems.

The methods that treat the electron correlation problem are continuously developing and evolving; many of these are based on the classical density distribution, while others take a wavefunction approach to the problem. Explicitly correlated methods, natural orbital methods, reduced density matrix methods, and also some simple empirical models are quite successful in predicting accurate correlation energies for large number of molecular systems. Several such models were described here, and their large advantage is their computational efficiency, which makes them applicable to a wide range of chemical systems.

There are several possible ways for the atomic correlation models described in this thesis to evolve and to improve their accuracy. For example, some of the future work

plans to use at the relationships between correlation energy and orbital energies, spatial coincidence, and the radial densities of the atomic orbitals.

It would be interesting to explore the changes in the calculated HF properties with the addition of an electron to a system and compare it to the changes in the corresponding correlation energy. The change in total correlation (dE_{corr}/dN) would not only include an additional correlation energy due to an extra electron (E_{corr_new}), but also the changes in the correlation energy corresponding to the electron pairs already present in the system ($\sum_{ab} \frac{dE_{corr\_ab}}{dN}$), and therefore to the properties of these electrons (equation 4.1). The changes in the Coulomb energy, kinetic energy, and changes in the exchange energy (Figure 4.1) might all be helpful in determination of the changes in the correlation energy. These changes are also expected to be related to the changes in the orbital energies ($d\varepsilon_{aa}$), so in the future, models related to the equations 4.2 and 4.3 could be explored:

$$\frac{dE_{corr}}{dN} = \sum_{ab} \frac{dE_{corr\_ab}}{dN} + E_{corr\_new} \tag{4.1}$$

$$E_{corr} \propto \sum_{a} \varepsilon_{aa} \tag{4.2}$$

$$\frac{dE_{corr}}{dN}(Z) \propto \sum_{a} \frac{d\varepsilon_{aa}}{dN} \tag{4.3}$$

The correlation energy depends not only on the size and the shape of the orbitals that describe the particular electron pair, but also it likely depends on the amount of space that these orbital share. While the size and the volume of an electron pair is related to the shape and size of a MO describing it, the overlap of these orbitals could be related

to their spatial coincidence or can be determined from the radial density function. Relating the correlation energy to such properties as radial density ($r^2R^2(r)$) or spatial coincidence (SPC) in addition to other HF orbital properties might prove useful, especially in determination of the correlation energy between the electrons in different orbitals or different shells:

$$E_{corr} \propto r^2R^2(r) \tag{4.4}$$

$$E_{corr} \propto SPC\ (r) \tag{4.5}$$

The empirical atomic correlation energy models can prove to be quite beneficial in gaining better understanding of the correlation energy problem in general. While it is desirable to solve the correlation problem for the atomic systems, there is much greater need to be able to apply or extend these models to a wide range of molecular systems. Future work will explore this applicability of the atomic correlation models to a large range of the molecular systems.

4.2. Molecular Models

The extension the atomic correlation energy models to molecular systems might be applicable in the modeling of some parts of the molecular correlation energy, such as the correlation energy of the core electrons of the constituent atoms. Total molecular correlation energy can be partitioned into the core-core correlation, core-valence correlation, and the valence-valence correlation, where the core-core correlation would be modelled using corresponding atomic system:

$$E_{corr} = \sum_{ab} E_{corr\_ab}^{core-core} + \sum_{ab} E_{corr\_ab}^{core-valence} + \sum_{ab} E_{corr\_ab}^{valence-valence} \qquad (4.6)$$

Koga *et. al.*[53] pointed out that the electron density at the nucleus is almost the same for each cation, neutral atom, and anion for the same atomic number *Z*. The electron density at the nucleus can be modelled as almost entirely due to the *s*-type atomic orbitals, predominantly the 1*s* orbital. Liu and Parr[44] extended this idea and related the electrostatic potential and the density at the nucleus to the correlation energy. It would be interesting to explore whether we can apply the calculated HF energy components corresponding to the core electrons of each constituent atom of the molecular systems and relate it to the core-core molecular correlation energy.

Mohajeri *et.al*[45] explored the extension of a simple atomic model to the molecules and by using the additivity scheme they derived the model for molecular correlation energies in terms of constituent atoms and the number of electrons. They confirm that the correlation energy in molecules is larger than the sum of the correlation energies of its corresponding constituent atoms, and even though their molecular model is not of

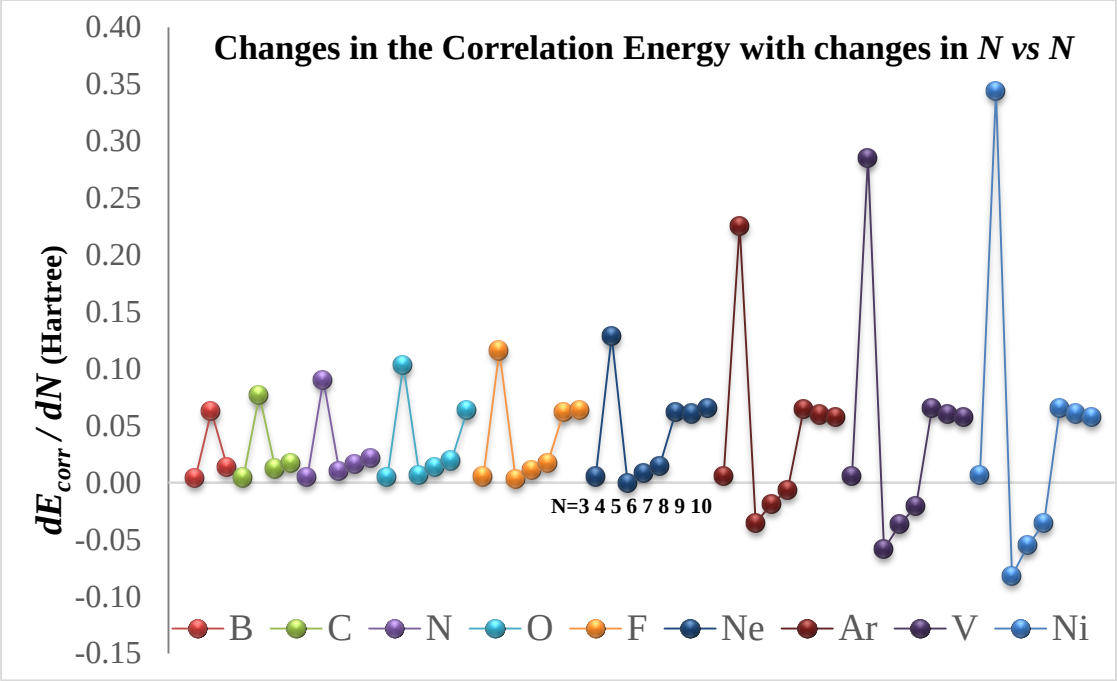
chemical accuracy, it is nevertheless useful and economical procedure to estimate correlation energies of closed-shell polyatomic systems.

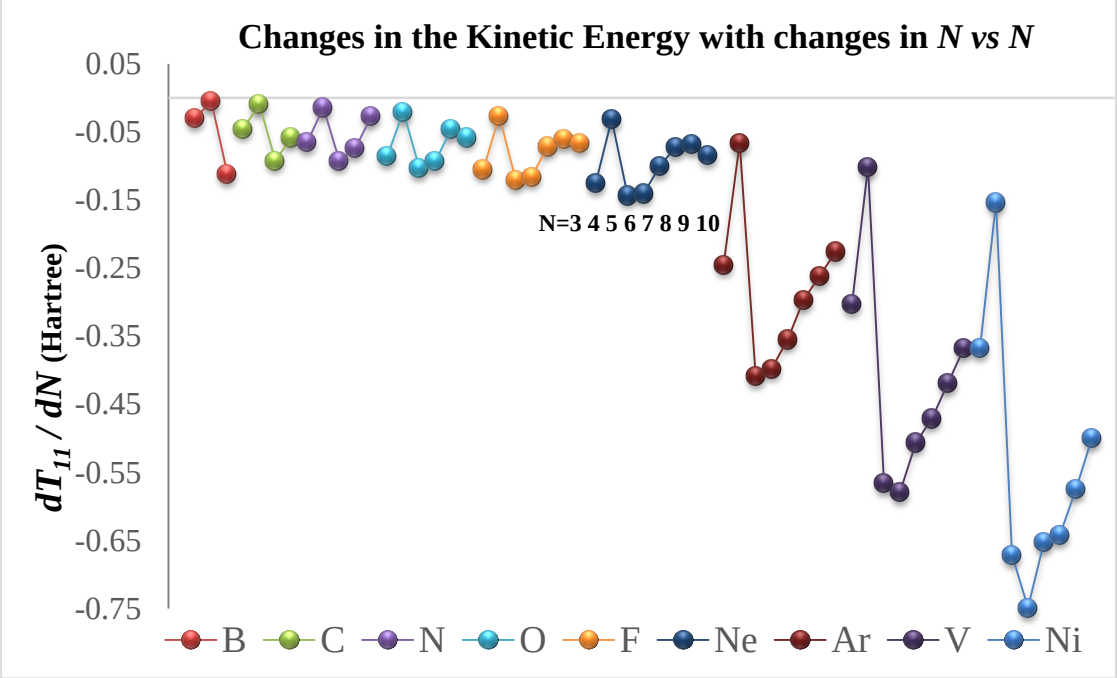
A possible extension of these models is to determine the HF properties corresponding to each atom in the molecule, and use the atomic correlation energy models described earlier to obtain the corresponding atomic correlation. The total molecular correlation energy could be obtained by adding the atomic correlations. The missing amount of interatomic correlation might be possibly determine from the properties of valence electrons predominantly involved in the bonding.

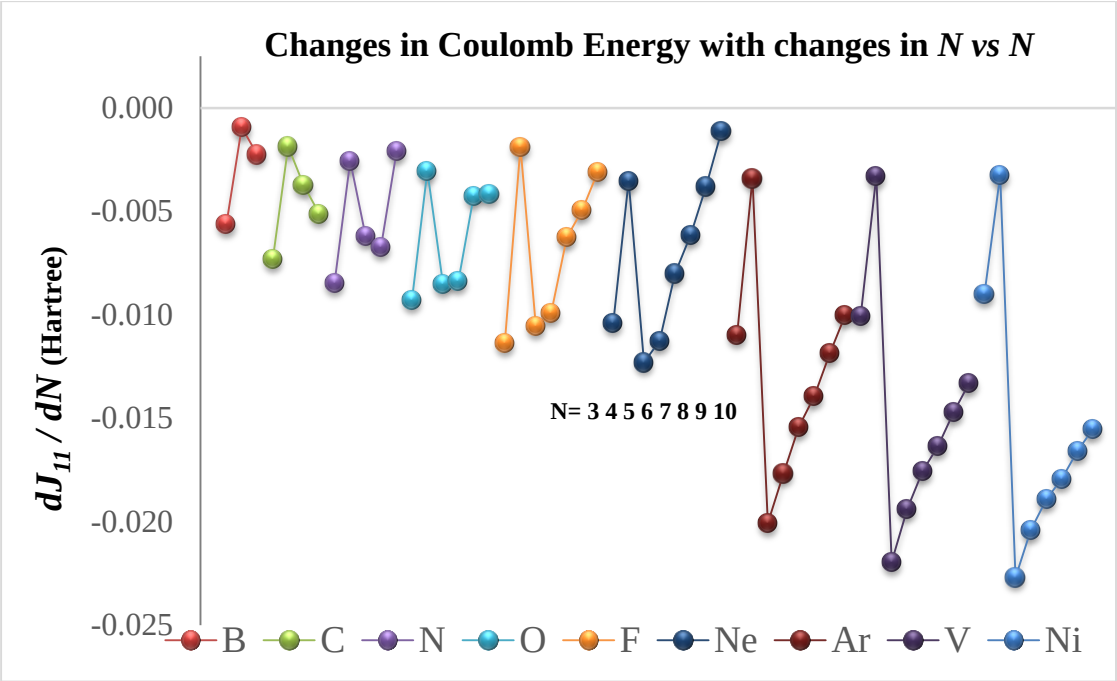
$$E_{corr} = \sum_{A,ab} E^{(A)}_{corr\_ab} + \sum_{AB,ab} E^{(AB)}_{corr\_ab} \tag{4.7}$$

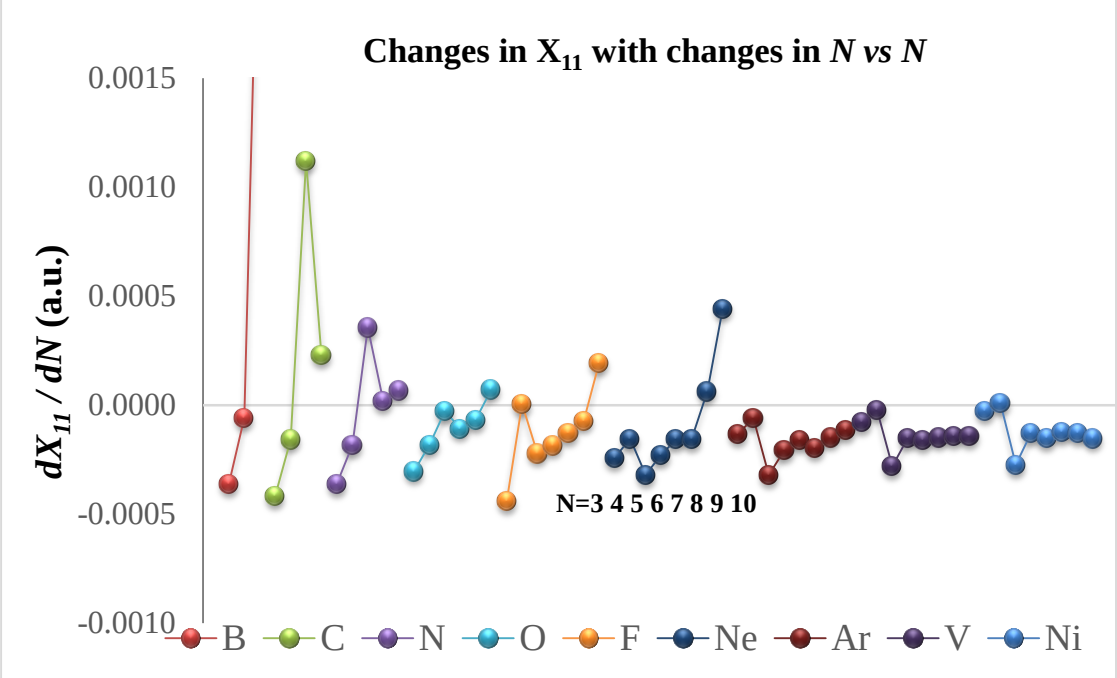
$$E_{corr} = \sum_{A,a} E^{(A)}_{corr\_aa} + \sum_{A,ab} E^{(A)}_{corr\_ab} + \sum_{AB,a} E^{(AB)}_{corr\_aa} + \sum_{AB,ab} E^{(AB)}_{corr\_ab} \tag{4.8}$$

Similar to the atomic systems, the properties such as the radial density or spatial coincidence (SPC) in addition to other HF molecular orbital properties might be useful in the approximation of the correlation energy between the electrons in different molecular orbitals.


Changes in the Correlation Energy with changes in N vs N
dE_corr / dN (Hartree)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
N=3 4 5 6 7 8 9 10
B C N O F Ne Ar V Ni


Changes in the Kinetic Energy with changes in N vs N
dT_11 / dN (Hartree)
0.05
-0.05
-0.15
-0.25
-0.35
-0.45
-0.55
-0.65
-0.75
N=3 4 5 6 7 8 9 10
B C N O F Ne Ar V Ni


Changes in Coulomb Energy with changes in N vs N
0.000
-0.005
-0.010
-0.015
-0.020
-0.025
dJ11 / dN (Hartree)
N= 3 4 5 6 7 8 9 10
B C N O F Ne Ar V Ni


Changes in X11 with changes in N vs N
0.0015
0.0010
0.0005
0.0000
-0.0005
-0.0010
dX11 / dN (a.u.)
N=3 4 5 6 7 8 9 10
B C N O F Ne Ar V Ni

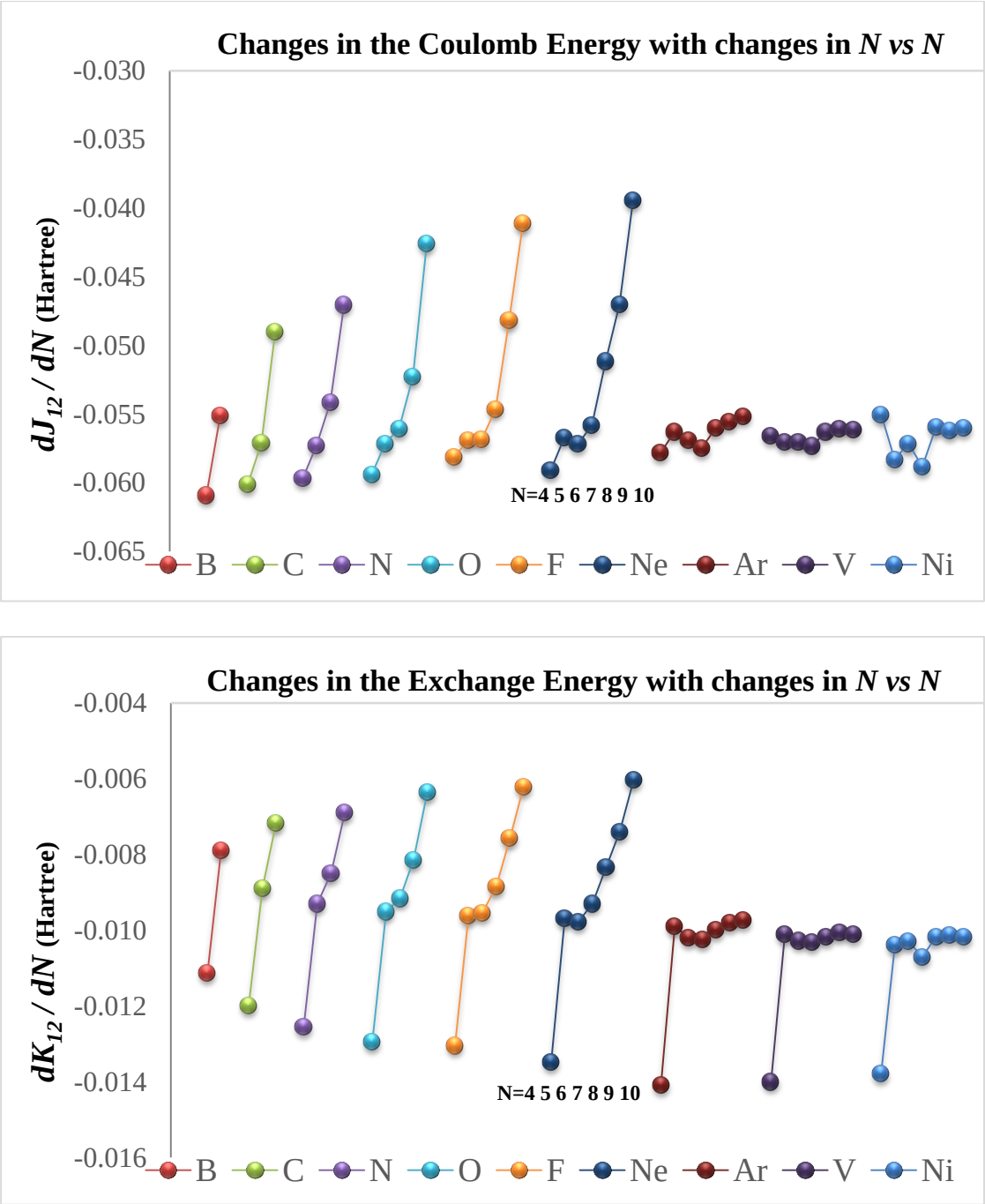


Figure 4.1. The changes in the correlation energy with *N* vs *N* compared to the changes in HF values of the Coulomb energy, kinetic energy and exchange energy with *N* vs *N* corresponding to the core electrons described by the $1s^2$ atomic orbital.

List of Models

$$E_{corr} = C_{aa}(N)\sum_{a} X_{aa}^{1\downarrow} + C_{ab}^{1\downarrow}(N)\sum_{ab} X_{ab}^{1\downarrow} + C_{ab}^{11}(N)\sum_{ab} X_{ab}^{11} + aZ$$

$$E_{corr} = C_{aa}(N)\sum_{a} X_{aa}^{1\downarrow} + C_{ab}^{1\downarrow}(N)\sum_{ab} X_{ab}^{1\downarrow} + C_{ab}^{11}(N)\sum_{ab} X_{ab}^{11} + aK_{12}$$

$$E_{corr} = \sum_{a} C_{aa}^{(N)} X_{aa} + \sum_{ab} C_{ab}^{(N)} X_{ab} + c(N)K_{12}$$

$$E_{corr} = \sum_{a} C_{aa} X_{aa} + \sum_{ab} C_{ab} X_{ab} + c(N)K_{12}$$

$$E_{corr} = C_I N + c_I$$

$$E_{corr} = C_{II}\sqrt{N_{\uparrow\downarrow pairs}} + c_{II}$$

$$E_{corr} = C_{III}\sqrt{\sum_{ab} J_{ab}} + c_{III}$$

$$E_{corr} = C_{IV}\sum_{ab} J_{ab}/\sqrt{T_{aa} + T_{bb}} + c_{IV}$$

$$E_{corr} = C_V\left(\textstyle\sum_{ab} J_{ab}/\sqrt{\sum_{a} T_{aa}}\right) + c_V$$

5. Bibliography

(1) Dirac, P. A. *M. Proc. R. Soc. Lond. Ser A.* **1929**, *123*, 714.

(2) Tew, D. P.; Klopper, W.; Helgaker, T. *J. Comp. Chem.* **2007**, *28*, 1307.

(3) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Publications: Mineola, N.Y., **1996**.

(4) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models.*; 2 ed.; John Wiley and Sons, Ltd., **2004**.

(5) Born, M.; Oppenheimer, R. *Ann. Physik* . **1927**, *84*, 457.

(6) Levine, I. N. *Quantum Chemistry*; 5 ed.; Prentice-Hall, Inc., **2001**.

(7) Hartree, D. R. *Math. Proc. Cambridge Philos. Soc.* **1928**, 24, 89.

(8) Hartree, D. R. *Math. Proc. Cambridge Philos. Soc.* **1928**, 24, 111.

(9) Slater, J. C. *Phys. Rev.* **1928**, *31*, 333.

(10) Slater, J. C. *Phys. Rev.* **1930**, *35*, 210.

(11) Fock, V. *Z. Phys. Rev.* **1930**, *61*, 126.

(12) Liberti, L.; Lavor, C.; Maculan, N.; Nascimento, M. A. C. *Discrete Applied Mathematics, Reformulation Techniques and Mathematical Programming* **2009**, 157, 1309.

(13) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(14) Shaik, S. S.; Hiberty, P. C. *Chemist's Guide to Valence Bond Theory*; John Wiley & Sons: Hoboken, NJ, USA, **2008**.

(15) Heitler, W.; London, F. *Zeits. für Physik* **1927**, *44*.

(16) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; 2 ed.; Wiley-VCH, **2001**.

(17) Fröman, A. *Phys. Rev.* **1958**, *112*, 870.

(18) Löwdin, P.-O. *Adv. Chem. Phys.* **1959**, *2*, 207.

(19) Beran, G. J.; Hirata, S. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7559.

(20) Hollett, J. W.; McKemmish, L. K.; Gill, P. M. *J. Chem. Phys.* **2011**, *134*, 224103.

(21) McCarthy, S. P.; Thakkar, A. J. *J. Chem. Phys.* **2011**, *134*, 044102.

(22) O'Neill, D. P.; Gill, P. M. W. *Mol. Phys.* **2005**, *103*, 763.

(23) Hättig, C.; Klopper, W.; Kohn, A.; Tew, D. P. *Chem. Rev.* **2012**, *112*, 4.

(24) Mok, D. K. W.; Neumann, R.; Handy, N. C. *J. Phys. Chem.* **1996**, *100*, 6225.

(25) Clementi, E.; Corongiu, G. *J. Mol. Struct. THEOCHEM* **2001**, *543*, 39.

(26) Hylleraas, E. A. *Z. Phys. A.* **1929**, *54*, 347.

(27) Hylleraas, E. A. *Z. Phys. A.* **1930**, *65*, 209.

(28) Davidson, E. R.; Hagstrom, S. A.; Chakravorty, S. J.; Umar, V. M.; Fischer, C. F. *Phys. Rev. A* **1991**, *44*, 7071.

(29) Chakravorty, S. J.; Gwaltney, S. R.; Davidson, E. R.; Parpia, F. A.; Fischer, C. F. *Phys. Rev. A* **1993**, *47*, 3649.

(30) Sinanoglu, O.; Pamuk, H. O. *J. Am. Chem. Soc.* **1973**, *95*, 5435.

(31) Bernardi, F.; Csizmadia, I.; Smith, V., Jr.; Whangbo, M. H.; Wolfe, S. *Theoretica chimica acta* **1975**, *37*, 171.

(32) Daudel, R.; Goddard, J. D.; Csizmadia, I. G. *Int. J. Quant. Chem.* **1977**, *11*, 137.

(33) Bernardi, F.; Mezey, P. G.; Csizmadia, I. G. *Can. J. Chem.* **1977**, *55*, 2417.

(34) Poirier, R. A.; Hollett, J. W. *J. Theor. Comp. Chem.* **2007**, 06, 13.

(35) Robb, M. A.; Haines, W. J.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1973**, *95*, 42.

(36) López-Boada, R.; Pino, R.; Valderrama, E. *J. Mol. Struct. THEOCHEM* **1999**, *466*, 197.

(37) Ang, M. H.; Yates, K.; Csizmadia, I. G.; Daudel, R. *Int. J. Quant. Chem.* **1980**, *20*, 793.

(38) Csizmadia, I. G.; Peterson, M. R.; Poirier, R. A.; Daudel, R. *Int. J. Quant. Chem.* **1981**, *19*, 25.

(39) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*, **1990**.

(40) Alonso, J. A., Cordero, N.A. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, 1629.

(41) Alonso, J. A.; March, N. H.; Cordero, N. A.; Rubio, A. *J. Phys. B: At. Mol. Opt. Phys.* **2003**, *36*, 2695.

(42) Gritsenko, O. V.; Cordero, N. A.; Rubio, A.; Balbás, L. C.; Alonso, J. A. *Phys. Rev. A* **1993**, *48*, 4197.

(43) McCarthy, S. P.; Thakkar, A. *J. Chem. Phys. Lett.* **2010**, *494*, 312.

(44) Liu, S.; Parr, R. G. *J. Phys. Chem. A.* **2007**, *111*, 10422.

(45) Mohajeri, A.; Alipour, M. *J. Mol. Struct. THEOCHEM* **2009**, *907*, 115.

(46) Koga, T.; Watanabe, S.; Kanayama, K.; Yasuda, R.; Thakkar, A. J. *J. Chem. Phys.* **1995**, *103*, 3000.

(47) Fock, V. *Zeits. für Physik* **1930**, *63*, 855.

(48) Rassolov, V. A. *J. Chem. Phys.* **1999**, *110*, 3672.

(49) Poirier, R. A.; Hollett, J. W.; Bungay, S. D.; Colonna, F.; El-Sherbiny, A.; Gosse, T.; Keefe, D.; Kelly, A.; Pye, C. C.; Reid, D.; Shaw, M.; Staveley, M.; Wang, Y.; Warburton, P. L.; Xidos, J. *MUNgauss (Fortran 90 version)*, **2010**.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Wallingford CT; Gaussian 09, Revision B.01, **2009**.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Laham, A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian 03, Revision C.02, **2003**.

(52) Rassolov, V. A. *J. Chem. Phys.* **2009**, *131*, 204102.

(53) Thakkar, A. J.; Koga, T. *Theor. Chem. Acc.* **2003**, *109*, 36.